

**ENVIRONMENTAL FATE OF SELECTED RICE
HERBICIDES (Thiobencarb and Molinate)
UNDER FIELD CONDITIONS**

APRIL 1984



ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

**State of California
Department of Food and Agriculture
Division of Pest Management, Environmental Protection & Worker Safety
Unit of Environmental Monitoring & Pest Management
1220 N Street, Sacramento, California 95814**

Environmental Fate of Selected Rice Herbicides (Thiobencarb
and Molinate) Under Field Conditions.

by

L.J. Ross, R.J. Sava and R.J. Oshima

April 1984

Field Monitoring: R.J. Sava, J. Franz, C. Garretson,
R. Sagawa, M. Wilkerson, F. Zalkin,
S. Simpson, N. Miller, D. Duncan

Statistics & Graphics: T. Younglove(1), L. Ross, L. Heath,
S. Wilson(1).

Sampling Methods and
Preparation: T.Mischke, V. Bunac, B. Winters

Chemical Analysis: R. Magkoski, J. Echelberg, I. Yanrz,
D. Dhoot, V. Vergava, K. Yuki,
J. Alexander, C. Wiskoff, T. Joe

Data/Word Processing: N. Miller, M. Wilkerson, C. Cardozo,
H. Margolis, C. Garretson, M. Hoversten,
J. Boursier.

1). Statewide Air Pollution Research Center
University of California at Riverside
Riverside, California 92521

ABSTRACT

Environmental fate of the rice herbicides, thiobencarb and molinate, was assessed using two methods. A mass balance budget was calculated to determine the relative concentration of herbicide in the air, water, soil and vegetation components of rice fields. In addition, inlet and outlet water flow rates plus companion herbicide concentrations were collected and used to calculate a linear regression equation predicting herbicide concentrations leaving a "typical" rice field.

The mass balance budget of thiobencarb showed this chemical to be persistent in water, soil and vegetation. Sixty-one % of peak soil concentration (2329 ppb) and 10% of peak vegetation concentration (169 ppb) was still present one month after thiobencarb was applied. In comparison, little thiobencarb was found in water at this time (8 ppb) because of dilution and mass flow of herbicide-laden water off the rice field. However, when thiobencarb-laden flood water was held for 6 days, concentrations did not drop significantly (t -test, $\alpha=.05$) and remained above 500 ppb. Under these study conditions, holding flood water for six days did not significantly reduce the concentration of thiobencarb in water.

Five rice fields were monitored for inlet and outlet water flow rates plus thiobencarb concentrations. Thiobencarb concentrations at field drains were correlated with the log of day post-application. The R^2 value for the linear regression equation was .73 and the standard error of the estimate (SEE) was 166 ppb. Since the SEE was high in comparison with the mean concentration of thiobencarb in water (204 ppb), and the R^2 was low, this equation would be best used as a descriptive rather than predictive tool.

In contrast to thiobencarb, molinate dissipated rapidly in water, vegetation and to some extent, soil. Thirty-one % of peak soil concentration (656 ppb) and 2% of peak vegetation concentration (21 ppb) was present one month after molinate application. After a 4 day holding period, molinate concentrations in water decreased 49% to 1756 ppb from the concentration present on the day of application. Under these field conditions, molinate concentrations in water declined significantly during the 4 day holding period (t -test, $\alpha=.01$).

The equation developed for predicting molinate concentrations at field drains has potential for practical use. In this equation molinate concentrations were correlated with the log of and square root of the day post-application. The R^2 value was .94 indicating an excellent fit of predicted points with observed concentrations. By multiplying these predicted concentrations by drain flow rates and extrapolating over the

total acreage sprayed with molinate, it would be possible to assess the mass discharge of molinate into drainage canals. This model was subsequently used to estimate an appropriate water concentration to further reduce molinate concentrations in the major agricultural drains.

ACKNOWLEDGEMENTS

This study was a combined effort of the California Department of Food and Agriculture, State Water Resources Control Board, Department of Water Resources, the University of California at Davis, various county agencies and many individuals in the private sector.

Partial funding for this study was administered by John Cornacchia, State Water Resources Control Board, Sacramento, California. These funds were provided through an Areawide Waste Treatment Management Continuing Planning Program grant from the U.S. Environmental Protection Agency, Region IX, under the provisions of Section 108 of the Federal Water Pollution Control Act, as amended.

We would like to thank: Dr. James Seiber, Jim Woodrow, and Mike McChesney, Environmental Toxicology Department, University of California, Davis, for design, implementation and calculation of evaporative flux from mass balance test fields; Sid Sakamoto, Chevron Chemical Co. for contributing Bolero 10G to treat the 92 acre test field; Robert McGill and Don Werner, Land and Water Use, Northern District of the Department of Water Resources for their time, knowledge and experience in measurement of rice field water flow and; Dr. Jim Hill and Steve Scardaci, Agricultural Extension Service, University of California, Davis, for sharing their time and knowledge of rice cultural techniques.

Special thanks are extended to the agricultural commissioners and staffs in Colusa and Glenn Counties for the use of a Stevens Staff Gauge for the duration of the study, and to Jack Campbell, Kanawa Irrigation District, for helping to identify suitable fields to monitor.

A special thank you to all the growers that granted permission to enter their property for the purpose of taking samples. Finally, we would like to express our sincere appreciation to Gordon Wylie, a most uncommon, cooperative grower and friend.

DISCLAIMER

The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such product.

TABLE OF CONTENTS

	Page
Abstract.....	i
Acknowledgements.....	iii
Disclaimer.....	iii
Table of Contents.....	iv
List of Figures.....	vi
List of Tables.....	viii
Introduction.....	1
Part I. Thiobencarb.....	4
Materials and Methods.....	4
A. Thiobencarb Mass Balance Procedures.....	4
B. Thiobencarb Flow Field Procedures.....	11
Results.....	17
A. Mass Balance.....	17
B. Flow Fields.....	27
Discussion.....	37
Part II. Molinate.....	41
Materials and Methods.....	41
A. Molinate Mass Balance Procedures.....	41
B. Molinate Flow Field Procedures.....	43
Results.....	50
A. Mass Balance.....	50
B. Flow Fields.....	58
Discussion.....	73
References.....	76
Appendix A. Determination of Evaporative Flux For Thiobencarb and Molinate Were Calculated by J.N. Seiber, J.E. Woodrow and M. McChesney in a Manner Similar to the Methods Described in the Following Report: "Measurement of Evaporative Flux of MCPA and Two Transforma- tion Products from a Commercial Rice Field...	78

	Page
Appendix B. Chain of Custody for Chemical Analysis.....	95
Appendix C. Chemical Analytical Methods for Thiobencarb, Molinate and Their Breakdown Products in Water, Soil, Vegetation and Air Samples.....	97
Appendix D. Chain of Custody for Flow Fields.....	109
Appendix E. Comparison of Thiobencarb and Molinate Concentrations in Air.....	111
Appendix F. Errata.....	113

LIST OF FIGURES

		Page
Figure 1.	Mass balance field (#3).....	5
Figure 2.	The paddy sampler.....	7
Figure 3.	The water sampler.....	7
Figure 4.	Complete sampling apparatus.....	7
Figure 5.	Flow field #7.....	13
Figure 6.	Flow field #9.....	13
Figure 7.	Flow field #13.....	14
Figure 8.	Flow field #14.....	14
Figure 9.	Thiobencarb concentration over time.....	18
Figure 10.	Thiobencarb phase partition coefficients.....	19
Figure 11.	Thiobencarb phase partition coefficients (air).....	20
Figure 12.	Mass alance budget of thiobencarb.....	21
Figure 13.	Flow, flux and concentration of thiobencarb flow field #7.....	28
Figure 14.	Flow, flux and concentration of thiobencarb flow field #9.....	29
Figure 15.	Flow, flux and concentration of thiobencarb flow field #10.....	30
Figure 16.	Flow, flux and concentration of thiobencarb flow field #13.....	31
Figure 17.	Flow, flux and concentration of thiobencarb flow field #14.....	32
Figure 18.	Observed () and predicted () thiobencarb concentrations at the drain of flow fields.....	35
Figure 19.	Mass balance field (#4).....	42
Figure 20.	Flow Field #1.....	44

	Page
Figure 21.	Flow field #6 and #5..... 45
Figure 22.	Flow field #8..... 46
Figure 23.	Flow field #11..... 47
Figure 24.	Flow field #12..... 48
Figure 25.	Flow field #16 and #17..... 49
Figure 26.	Molinate concentration over time..... 51
Figure 27.	Molinate phase partition coefficients. 52
Figure 28.	Molinate phase partition coefficients (air)..... 53
Figure 29.	Mass balance budget of molinate..... 55
Figure 30.	Flow, flux and concentration of molinate flow field #1..... 60
Figure 31.	Flow, flux and concentration of molinate flow field #5..... 61
Figure 32.	Flow, flux and concentration of molinate flow field #6..... 62
Figure 33.	Flow, flux and concentration of molinate flow field #8..... 63
Figure 34.	Flow, flux and concentration of molinate flow field #11..... 64
Figure 35.	Flow, flux and concentration of molinate flow field #12..... 65
Figure 36.	Flow, flux and concentration of molinate flow field #15..... 66
Figure 37.	Flow, flux and concentration of molinate flow field #16..... 67
Figure 38.	Flow, flux and concentration of molinate flow field #17..... 68
Figure 39.	Observed () and predicted () molinate concentrations at the drain of flow fields..... 71

LIST OF TABLES

		Page
Table 1.	Analysis of Variance Design for the Water, Soil and Vegetation Components of Mass Balance Field #3.....	9
Table 2.	Conditions Under Which Samples Were Transported and Stored.....	12
Table 3.	Analysis of Variance Results of Thiobencarb and Its Sulfoxide Breakdown Product.....	23
Table 4.	Statistical Analyses of Thiobencarb and Sulfoxide Concentrations in Water..	24
Table 5.	Statistical Analyses of Thiobencarb Concentrations in Soil and Vegetation..	25
Table 6.	Thiobencarb Flow Field Regression Equations.....	33
Table 7.	Thiobencarb Mass Discharge From Flow Fields.....	36
Table 8.	Statistical Analyses of Molinate and Sulfoxide Concentrations in Water.....	56
Table 9.	Statistical Analyses of Molinate Concentrations in Soil.....	57
Table 10.	Statistical Analyses of Molinate Concentrations in Vegetation.....	59
Table 11.	Molinate Flow Field Regression Equations.....	70
Table 12.	Molinate Mass Discharge From Flow Fields	72

INTRODUCTION

The United States produces 1.7% of the world's rice on only 0.9% of the world acreage devoted to rice (1). This high productivity is due largely to the technology available to the American rice grower in areas of land preparation, pest control, fertilization, irrigation water management and harvesting. Nowhere else is this advanced technology more evident than in California.

California contributes 24% of the United States' production of rice. In 1979, the yield per acre in California was 50% greater than the average yield in other rice producing states (2). Within California, most of the rice is grown in the Sacramento and San Joaquin Valleys. The dense clay and hardpan soils found in these areas make them ideal for rice production and less suitable for many other crops. These impervious layers reduce the downward percolation of water making it easier to keep the rice field continually flooded during the hot dry growing season.

Water management is a critical factor in the production of rice. Weed control, nutrient levels and crop vigor are all dependent on water management practices. Among all rice agricultural practices, water management exhibits the most variability from grower to grower. Water within a field may be static, as in periods of time when pesticides are applied, or flowing, as it is during most of the growing season. The water level within a field or paddy system may be maintained anywhere from 2 to more than 6 inches. The level in each paddy is regulated by a series of removable boards called rice boxes. These boxes are placed in the checks between pads and allow water to flow from one pad to another, regulating the water level within a field.

The use of herbicides is one of the major factors contributing to the high yield of rice fields in the United States. Herbicides such as thiobencarb and molinate (marketed as Bolero and Ordram, respectively) are used to control graminaceous weeds (particularly Echinochloa crus-galli, barnyard grass). Barnyard grass at an average of 3.5 plants per square foot over 92% of the rice acreage may reduce yields by as much as one third (3). Problems with barnyard grass increased with the switch from tall to short statured rice varieties in the late 1970's. Reduced plant height of short statured rice leads to decreased shading and a shallow water requirement, both factors contributing to the increase in the barnyard grass population (4). With the increase in acreage planted with short statured rice, the use of Ordram also increased. In 1981, Bolero became available for limited use. In 1982, more than 2 million lbs of herbicides (mostly Ordram and Bolero) were applied to rice in the

Sacramento Valley (5).

The granular formulations of thiobencarb and molinate are usually aerially applied to flooded rice fields when plants are in the 1 to 3 leaf growth stage. After application, flood water is held for 6 days (after thiobencarb application) or 4 days (after molinate application) on the field then released into drainage canals. In the Sacramento Valley, nearly all rice fields drain along a 65 mile stretch between Colusa and the confluence of the Feather and Sacramento Rivers. Studies conducted by the Department of Fish and Game and the University of California at Davis have shown that thiobencarb and molinate accumulate seasonally in water, sediment and biota of drainage and river waterways (6 & 7). Molinate and thiobencarb were discovered in the Sacramento River and delta in 1982 (5), and the discharge zone was shown to extend over 50 miles in these areas. The detection of these herbicides in the Sacramento River was not surprising since in low-flow years, about 40% of total river flow (measured at Knights Landing) comes from these agricultural drains (5).

The presence of thiobencarb and molinate in agricultural drainages, rivers and delta areas may potentially effect domestic water sources and recreational fishing resources. A bitter taste in Sacramento city drinking water during the rice growing season has been attributed to rice herbicides (8), particularly Bolero. Extensive fish kills in agricultural drains from 1980 to 1982 have been attributed to Ordram (9 & 10). A study concerning the effects of these herbicides in combination indicated a synergistic effect of Bolero and Ordram on fish mortality (cited in 8). At the State Environmental Hazards Assessment Committee meeting on Jan. 25, 1984, most investigators agreed that additional research is needed concerning these herbicides.

The occurrence of these herbicides in drains and rivers has raised questions regarding the control of herbicide concentrations found in these waterways. A reasonable point of control is at the rice field drains (5). Information concerning the environmental fate of these herbicides at that interface is inadequate. This project was designed to determine the distribution of thiobencarb and molinate in rice fields during the 6 and 4 day holding periods, respectively, and their movement into drainage canals after the release of flood water. The effectiveness of each holding period in reducing herbicide concentrations in water was assessed as well as a mass balance budget and an estimate of mass discharge of herbicide from a "typical" rice field. This information can then be integrated with data collected in drainage canals and rivers so that appropriate measures to mitigate environmental hazards associated with these herbicides can be established.

Part I of this report will discuss the environmental dynamics of thiobencarb, (S-(4-chlorophenyl)methyl diethylcarbamothioate). Part II will discuss molinate (S-Ethyl

hexahydro-1-h-azepine-1-carbothioate), with the same considerations.

Part I. Thiobencarb

Materials and Methods

A. Thiobencarb Mass Balance Procedures.

A 92 acre field (37 hectares) located in Glenn County, was chosen for the mass balance portion of this study. This field was divided into 6 pads or paddies (Fig. 1), and was scheduled for application of thiobencarb. The first pad (at the site of water inflow) was not seeded and served as a water warming pad. Field #3 had a single inlet and drain, simplifying water flow measurements. In the study area, thiobencarb was applied by aircraft when rice seedlings were in the two leaf stage, approximately 10 days after seeding. The application rate was 40 lbs. per acre of Bolero 10G (Chevron Chemical Co.) which contains 10% active ingredient (thiobencarb) and 90% inert ingredients.

Water measurement instruments used to monitor flow rates were placed at the inlet and outlet of field #3 and were maintained by personnel from the Department of Water Resources (DWR). Inflow was measured using an 18 inch McCrometer water meter. Cumulative flow readings were recorded once every 24 hours to document the volume of water delivered to the field. Outflow readings were obtained using a V-notch weir in combination with a Stevens stage recorder. Outflow rate could be determined instantaneously by reading the weir gauge or cumulatively from the Stevens recorder (11).

Continuous recordings of wind speed, wind direction, humidity and air temperature were documented using MET-1 meteorological stations. These weather instruments were positioned at the northern border of field #3, 18 feet (5.5 m) above ground level, during the study except May 28 through June 4. At this time, weather instrumentation was relocated to a portable pier constructed in the center of the field, and was positioned 6 ft (1.8 m) above the water surface. An additional anemometer for horizontal wind speed was installed 1 ft (.3 m) above the water surface. (For location details, see Figure 1.) This set-up enabled the gathering of data for evaporative flux measurements (see below) as well as for weather monitoring.

Sixteen sample sites were established for the thiobencarb mass balance field (Fig. 1). These sites were evenly divided among 4 pads: the first or inlet pad, the last, or drain pad, and two pads randomly chosen from the remaining portion of the field. All sampling locations were approximately 10 to 20 ft (3

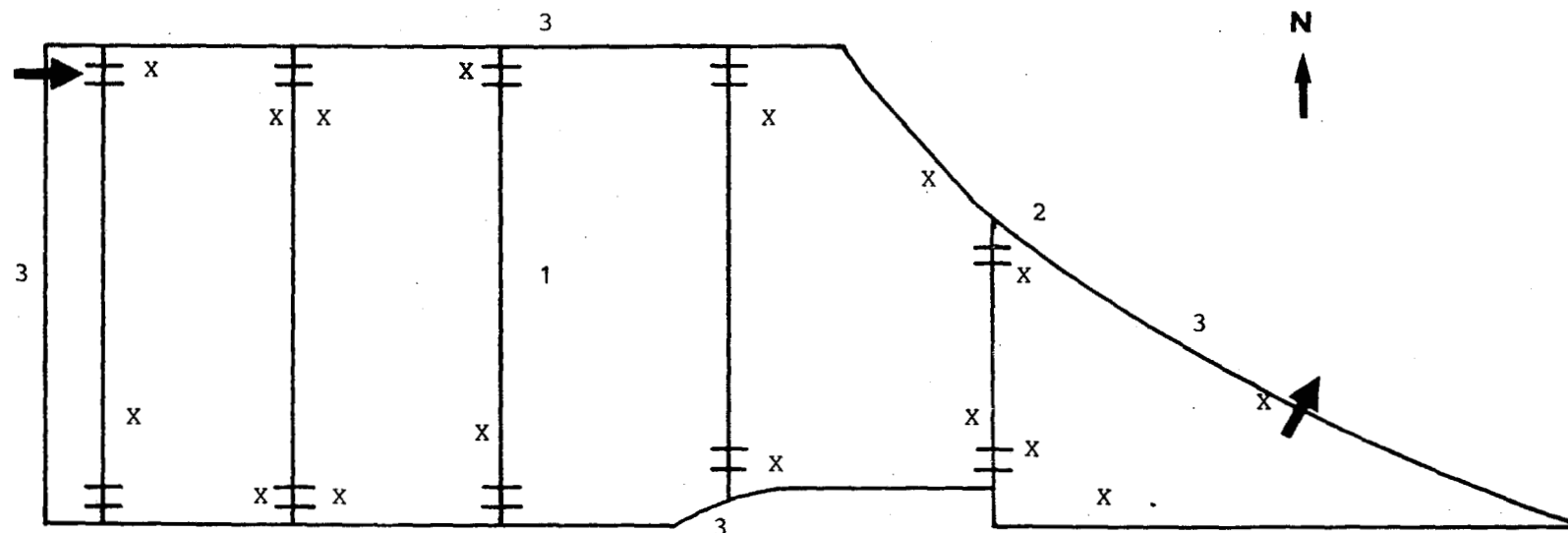


Figure 1. Mass balance field (#3) is 92 acres (37.2 hectares). Thiobencarb was applied 5/30/83 at 4 lbs. active ingredient/acres (AI/A). X = location of sample sites. 1 = location of weather instrumentation during evaporative flux measurements (5/18 through 6/4). 2 = location of weather instrumentation for the balance of the study. 3 = location of Hi-volume air samplers. Arrows indicate field water inlet and outlet.

to 6 m) from a check, and alternated from 20 to 100 ft (6 to 31 m) from the border of the field. Sample sites were located relative to the rice boxes to divide the sites between areas where water channeling occurred and areas of minimal water movement. From each of the 16 sites, water, vegetation, soil and herbicide deposition samples were collected for chemical analysis of thiobencarb and its sulfoxide break-down product. In addition to these 16 sites, water samples taken from the field inlet and drain were also analyzed for thiobencarb and sulfoxide.

A paddy sampler (Fig. 2) was constructed to delineate a 1 ft² area for sampling water, soil and vegetation. The sampler was carried to the sampling site and positioned in an area that was not previously sampled. This was accomplished by visually selecting an area where rice plants were present. The sampler effectively isolated the 1 ft² area and prevented mixing of water with mud. A water sampling device (Fig. 3) was also constructed that could draw a water sample from within the confines of the paddy sampler without disturbing the soil surface or aerate the water. The water sampler had to operate effectively in water depths from 2 to 8 in (1 to 16 cm). The water sampler as it was used with paddy sampler is depicted in Figure 4.

At each sample site, the paddy sampler was pushed approximately 4 in (10 cm) into the mud. The water sampling device, sample bottles and other necessary items were placed in a styrofoam floater to allow the use of both hands during sample collection. Prior to collection of water from a given site, the water sampling device was rinsed by pumping 10 to 14 oz (300-400 ml) of water from that site through it. A 1 l bottle was then attached to the water sampler and filled to capacity. The bottle was detached from the apparatus, topped off with water from the site and sealed with a teflon or aluminum foil-lined cap. When collecting a water sample from a site deeper than 8 in, the intake portion of the sampler was moved vertically through the water profile as the bottle was filling. This procedure provided a water sample representative of all water depths at a given site.

Water samples were always collected prior to vegetation or soil samples in an effort to minimize mixing of upper soil layers. Water samples were collected on the day before application (background), day of application (30 minutes after completion of application) and on post-application days 2, 4, 6, 8, 16 and 32. Inlet and outlet water samples were collected on the same schedule by immersing sample bottles directly in the water flow.

Vegetation samples were collected simultaneously with water samples. After the water sample was collected, the paddy sampler was left in place and all vegetation, (including roots), was removed and rinsed in water from the site. The vegetation was placed in a 500 ml amber glass jar and sealed with a teflon or

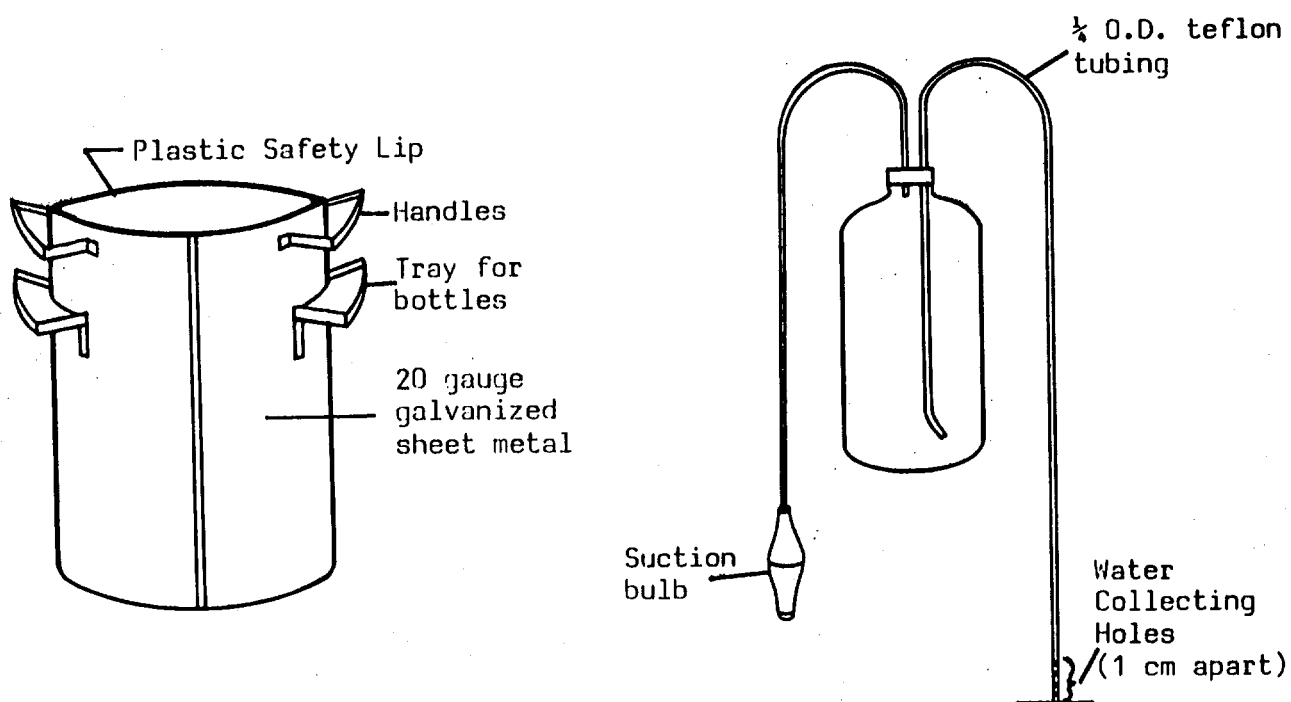


Figure 2. The paddy sampler is 18 in. (46 cm) in height and 13.5 in. (34 cm) in diameter.

Figure 3. The water sampler consists of a 1 L amber glass bottle, suction bulb, and teflon tubing with water collection holes.

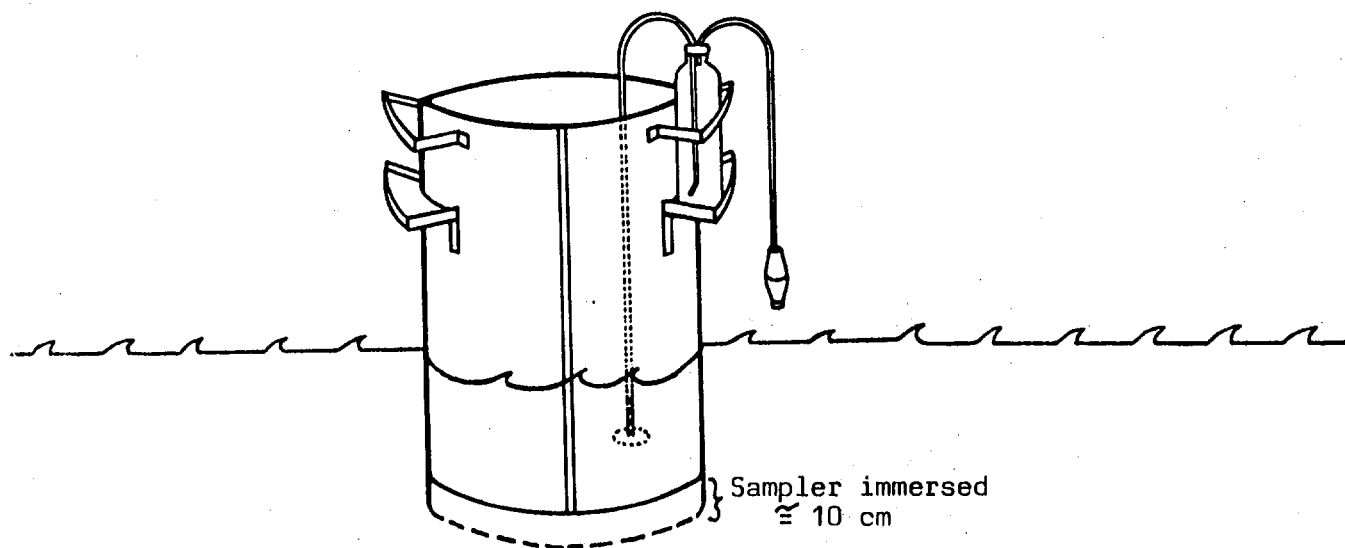


Figure 4. Complete sampling apparatus showing water and paddy samplers positioned in a flooded rice field.

foil-lined cap. Early in the growing season, when vegetation was sparse, it was necessary to collect from an area greater than 1 ft² to obtain a sample of sufficient mass to perform chemical analyses. At later sampling dates (16 and 32 days post-application), the opposite situation occurred and the sample submitted often represented some fraction of the sampling area.

Soil samples for each site were collected immediately after the vegetation samples. At times when it was necessary to reposition the paddy sampler for vegetation sampling, soil samples were only removed from the first sampling position. A stainless steel cylinder 6 in (15 cm) long and 3 in (7.6 cm) in diameter was pushed vertically 2 in (5 cm) into the sediment, tilted sideways to retain soil and remove excess water, and poured into a 1 quart Mason jar. The jars were then sealed with teflon or foil-lined lids. Four sediment plugs, taken at positions "3, 6, 9 and 12 o'clock" on the inside periphery of the paddy sampler, comprised a single sample of approximately 24 oz (700 ml).

To determine if significant changes occurred in thiobencarb and sulfoxide concentrations found in water, soil and vegetation, analysis of variance (ANOVA) tests were conducted. The 16 sampling sites (4 sites nested within each of the 4 paddies) were monitored on 7 different occasions (0, 2, 4, 6, 8, 16 and 32 days post-application). The experimental design for this is given in Table 1. Differences in thiobencarb and sulfoxide concentrations among days, among paddies and among sites were tested for. Also tested for were interactions between sites x days and sites x paddies. A Duncan's Multiple Range test (DMRT) was conducted on significant treatments. In addition to DMRT, two t-tests examined specific, a priori contrasts. The first compared 2 vs 6 days post-application. Since the holding period for thiobencarb was 6 days, we wanted to determine if concentrations changed significantly during that period. Day 0 was not used in the water comparison because thiobencarb does not readily dissolve in water (solubility = 30 mg/l at 20 C) and concentrations on that day would be low because of this. Similarly, it was believed that vegetation and soil samples would not have incorporated maximum thiobencarb concentrations on day 0. The second t-test compared 8 vs 32 days post-application. This was designed to test for a change in thiobencarb concentrations after the holding period. The t-statistic was calculated using the following formulas:

$$t' = d/s$$

$$s = \sqrt{s^2/n_1 + s^2/n_2}$$

$$d = \bar{x}_1 - \bar{x}_2$$

where s = combined standard deviation, s² = variance, n = sample size, \bar{x} = mean, d = difference between the two means being

Table 1. Analysis of Variance Design for the Water, Soil and Vegetation
Components of Mass Balance Field #3.

<u>Source of Variation</u>	<u>Degrees of Freedom</u>
Paddy	3
Day	6
Error	18
Site	3
Site x Day	18
Site x Paddy	9
Error	54
Total	111

compared and $t' = t$ -statistic (12). The t -statistic was compared with a tabulated t value with 6 degrees of freedom ($n_1 + n_2 - 2$).

Air samples were collected from the field perimeter using high volume (Hi-vol) air samplers (General Metals Works) to determine the concentration of thiobencarb in air. Each air sampler was equipped with a constant flow controller (Kurtz Instruments) calibrated at 30 cubic feet per minute. Air was drawn through a 4 in (10 cm) diameter glass cartridge packed with pre-cleaned XAD-2 macroreticular resin. Air samplers were centrally located at north, south, east and west borders of a field, approximately 2 ft (0.6 m) from the water's edge (Fig. 1). Air samples were taken 1 day before application (background), during application, immediately following application and on post-application days 2, 4 and 6. The sampling period for background and post-application days was 3 h; the sampling period for the day of application was the duration of application (ca. 1 h) plus 30 min. The 4 samplers were used to determine the drift of thiobencarb from the test field.

In addition to air samples gathered by our field monitoring crew, Dr. James N. Seiber (University of California at Davis) collected additional air samples for the use in evaporative flux calculations. (See Appendix A for methodology.) These calculations were then used in the mass balance budget to determine the relative amount of thiobencarb in air vs other components (water, soil and vegetation).

Samples of herbicide deposition quantified the actual amount of material impacting the test field as compared with a theoretical application of 40 lbs/acre. Herbicide deposition samples were collected the day thiobencarb was applied to the mass balance field. Samplers consisted of a pre-weighed polyethylene bag attached to a wire frame. The opening of the bag was 1.09 ft². Samplers were placed at each of the 16 paddy sites and were collected immediately upon completion of thiobencarb application. Mass deposition was calculated by re-weighing each sample bag and subtracting the original bag weight. The resulting difference was the amount of thiobencarb impacting the area of the bag opening. This was then extrapolated to the entire field.

Using evaporative flux computations, and soil, water and vegetation thiobencarb and sulfoxide concentrations plus herbicide deposition measurements, a mass balance budget was calculated. To determine the relative contribution of each medium (or component) to the total budget, the following formulas were used:

$$\text{Kg of thiobencarb in a solid medium} = \frac{(d)(v)(c)}{1 \times 10^{12}}$$

where d = density of that medium in g/cm³
 v = volume of that medium in cm³
 c = concentration of that medium in ng/g

Soil volume = depth of soil sampled x area of the field;
vegetation volume = average canopy height x area of the field.

$$\text{Kg of thiobencarb in water} = \frac{(v) (c)}{1 \times 10^9}$$

where

v = volume of water in liters

c = concentration of water in ug/l

Water volume = depth of water x area of the field.

Once the weight of thiobencarb partitioned into each medium was calculated, these weights were divided by the total weight of herbicide deposited on the field, (as estimated from the mass deposition samples collected), to determine the relative proportion of each component to the total budget.

The handling and storage of various types of media sampled is described in Table 2. Due to the large number of samples collected, and the anticipated 4 month storage period, it was necessary to add 20-30 g non-reagent grade sodium chloride to the water and soil samples in order to minimize the breakdown of thiobencarb. Water samples were analyzed first, followed by soil, vegetation and air samples. This order of priority allowed the samples most susceptible to degradation to be analyzed first (water and soils could not be frozen while in storage). Also, concentrations of thiobencarb often approached minimum detection levels in water samples making it logical to analyze water first.

Each sample collected was accompanied by a chain of custody form documenting the sequence of transfers from sample preparation through chemical analysis (Appendix B). Every individual who handled the sample was required to sign and date the form, acknowledging receipt and relinquishment of the sample. This form was also designed for recording data and results of chemical analyses to be entered into computer files.

All chemical analyses were performed by the Department of Food and Agriculture Chemical Laboratory, Sacramento, California. For specific analytical methods for water, soil, vegetation and air, refer to Appendix C.

B. Thiobencarb Flow Field Procedures

Five fields in Glenn and Colusa counties were chosen to monitor for the concentration of thiobencarb in water draining from rice fields. Figures 5 through 8 depict layouts of these fields. Fields were chosen based on three factors; anticipated use of thiobencarb for weed control in the 1983 season, ability to accurately measure inlet and outlet water flows and, growers'

Table 2. Conditions Under Which Samples Were Transported and Stored.

<u>Sample Type</u>	<u>Field to Laboratory Transport</u>	<u>Storage</u>
Water	Wet ice (4°C)	Salted, 4°C
Vegetation	Wet ice (4°C)	Rinsed in distilled water 5 times, trans- ferred to rinsed bottled, frozen at 20°C
Soil	Wet ice (4°C)	Salted, 4°C
Air	Dry ice (-70°C)	-20°C
Herbicide Deposi- tion	Dry ice (-70°C)	-20°C

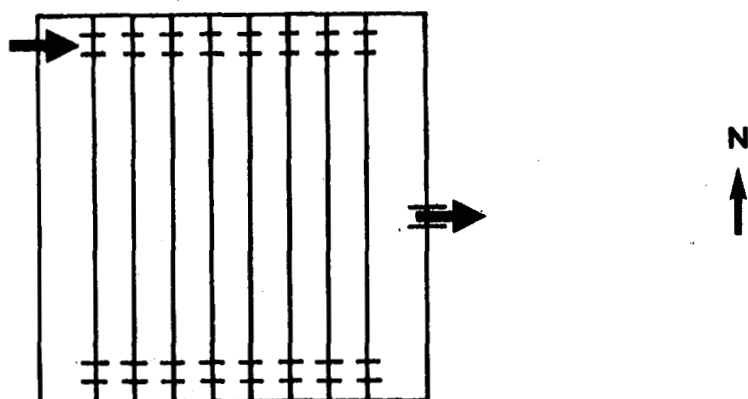


Figure 5. Flow field #7 is 40.5 acres (16.4 hectares). Thiobencarb was applied 5-25-83. Arrows indicate field water inlet and outlet.

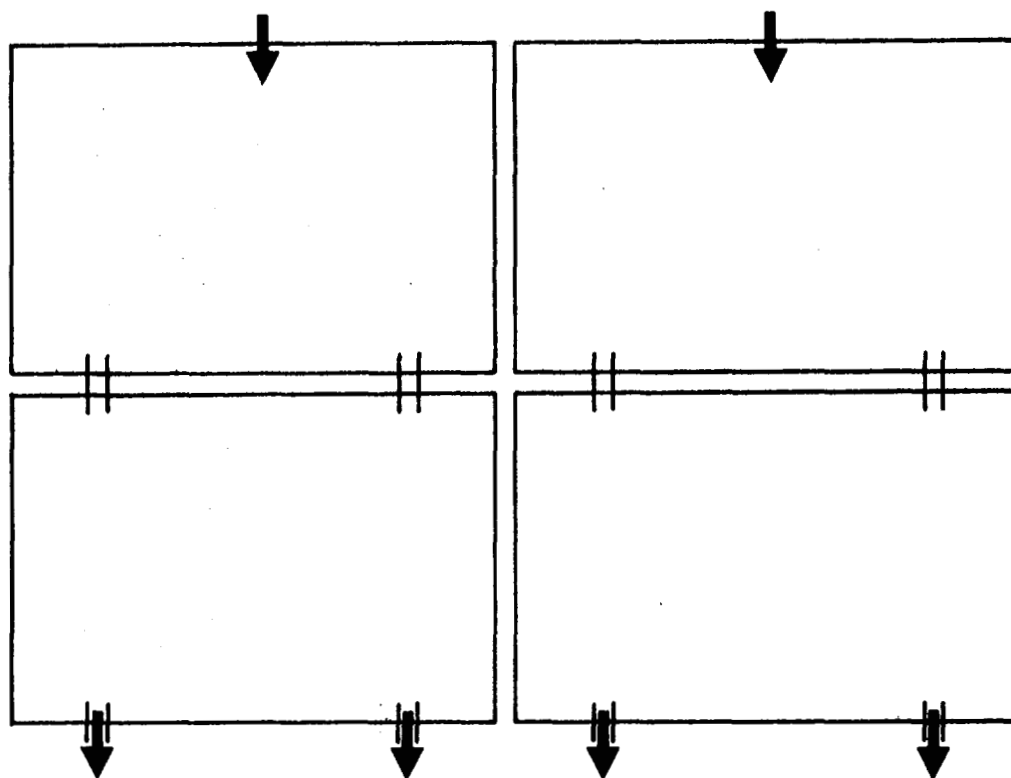


Figure 6. Field #9 (on the left) and field #10 are both 80 acres (32.4 hectares). Thiobencarb was applied 5-24-83. Arrows indicate field water inlet and outlet.

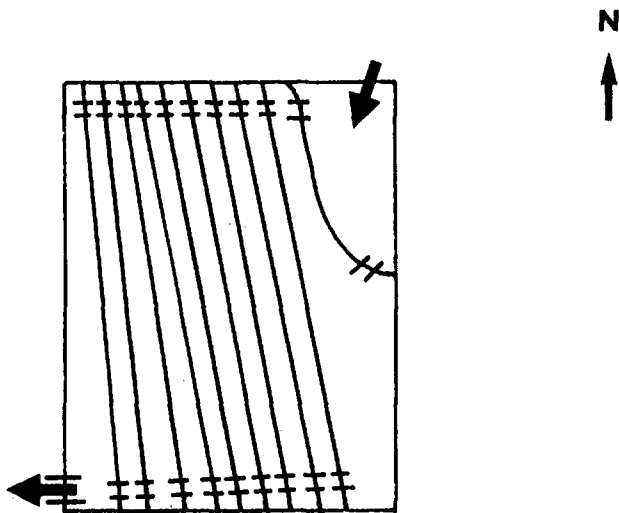


Figure 7. Field #13 is 30 acres (12.1 hectares). Thiobencarb was applied 5-28-83. Arrows indicate field water inlet and outlet.

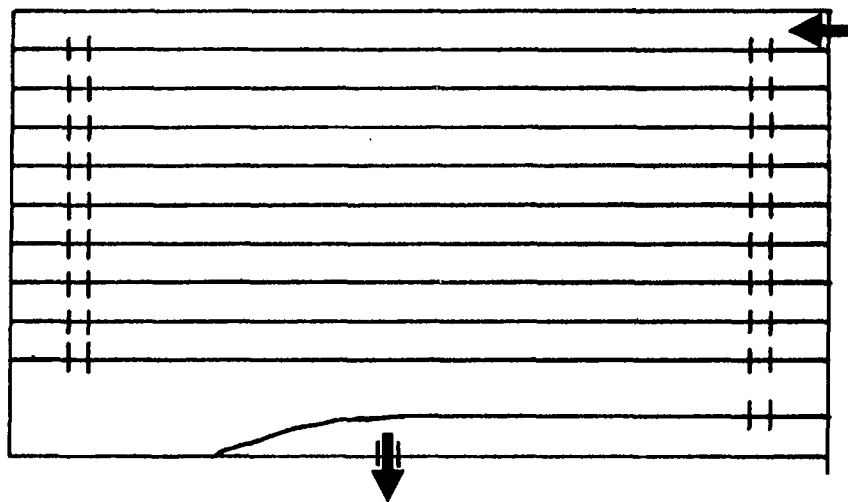


Figure 8. Field #14 is 90 acres (36.4 hectares). Thiobencarb was applied 5-28-83. Arrows indicate field water inlet and outlet.

written permission granting access to these fields.

Water flow measurements (into and out of each field) were initiated when rice first germinated (prior to herbicide application). Subsequent readings were taken at 3 day intervals until 30 days post-application. All flow measurements reported are single, instantaneous readings.

The original protocol for measuring water inflow involved the use of inlet gate valves for which water flow measurement tables were available. Due to a number of factors, the accurate measurement of gate valve flows was not possible. Therefore, inlet water flow rates were determined by summing the water flow over each rice box that separated the highest pad (pad #1) from the next highest pad. Stevens staff gauges were used to measure these flows.

Outlet flow was measured by using a Stevens staff gauge. All flow measurements were recorded on flow data sheets (Appendix D). In addition to staff gauge readings and weir width, water depth, water temperature, air temperature and relative humidity were recorded. For fields with multiple outlets, the volume of water draining from a field was considered to be the sum of all respective readings. At times when a field had zero flow or was in a holding period, a seepage measurement was calculated instead by determining the amount of time needed to fill a sample bottle.

Water samples were collected at the inlet and outlet sites of each field and were analyzed for the concentrations of thiobencarb and sulfoxide. (See Appendix D for chemical analysis.) These water samples were collected when flow measurements were made. Information recorded at sampling time included field water depth, water temperature, air temperature and relative humidity. Inlet water samples were collected from source canals or ditches as close as possible to the field entry point. Samples were collected by immersing a 1 l bottle below the water surface. To reduce the rate of volatilization of herbicide, the bottle was topped off with water from the sampling site and then sealed with aluminum foil-lined caps. Outlet water samples were collected from field drains and/or weirs by placing a 1 l bottle directly in the water flow. When water was not flowing over drain weirs, any water seeping out was collected. Water samples were transported and stored as in Table 2.

These five fields (termed, flow fields) were monitored to develop a regression equation predicting thiobencarb flux into drainage canals. Flux was defined as the concentration of thiobencarb at the drain (ppb = $\mu\text{g/l}$) times the drain flow rate (l/sec) divided by the field size (hectares). Flux was therefore measured in $\mu\text{g/sec/hectare}$, the amount of thiobencarb leaving a field per unit area. If an accurate equation could be developed, prediction of thiobencarb flux into drainage would be possible simply by knowing the amount of acreage sprayed with the

herbicide.

The BMDP stepwise linear regression program (13) was used to calculate the least squares equation. Independent variables entered into the program included; days post-application (days), drain flow rate (DFR), volume of water on a field, net flow rate (DFR minus inlet flow rate), days squared, days cubed, DFR squared, and DFR cubed. Each of the five fields was run through the program separately. If good agreement occurred among the resultant equations, then all raw data would be averaged and a single regresssion equation developed from that information.

RESULTS

Dry hot summers are typical of rice growing regions in Glenn and Colusa counties. Weather data collected May 29 through July 20 indicated that daytime highs averaged 31°C, nighttime lows averaged 17°C, with the average high relative humidity of 81% and average low of 30%. Prevailing winds were out of the north or south with wind speeds between 3.5 and 12.4 mph. These weather conditions are representative of other areas in the Sacramento Valley.

MASS BALANCE

Results from chemical analysis of air, water, soil and vegetation sampling are shown in Figure 9. Soil samples contained the highest thiobencarb concentrations. Soil concentrations reached a peak on day 6 of 3858 ppb. Soil concentrations declined on day 8 yet remained above 2000 ppb through the rest of the month. Air samples (taken 64 in or 163 cm above the water surface) peaked on the day of thiobencarb application at .06 ppb and declined below the minimum detectable level (MDL = 5 ug/air sample) on day 6 (Appendix E). No samples were collected beyond day 6. Vegetation samples reached peak concentration (1754 ppb) on day 4 and declined to 169 ppb on day 32. Water concentrations were lower than vegetation, with a high of 575 ppb on day 4 and a decline to 8 ppb on day 32.

Phase partition coefficients (Figs. 10 and 11) exemplify the relationship between 2 materials. A phase partition coefficient is merely the ratio of herbicide concentrations found in 2 mediums (14). The soil/water coefficients (Fig. 10) indicated that thiobencarb was preferentially held in soil vs water over time. This ratio was probably influenced by the replacement of thiobencarb-laden water with uncontaminated water. The vegetation/water coefficients (Fig. 10) indicated a partitioning of thiobencarb into vegetation (vs water) during the sampling period. However, most of the coefficients were near 2 up until day 16 where they increased. The pattern of soil/vegetation coefficients was similar to that of soil/water. The air/water and air/vegetation coefficients (Fig. 11) were all well below 1 and declined over time. Air/soil coefficients were not calculated since none of the thiobencarb in air was expected to evaporate from soil since the soil was covered with water during air sampling.

Results from the mass balance calculations are shown in Figure 12. On days 2, 4 and 6 we recovered 70-74% of the applied thiobencarb. On day 0, only 43% was accounted for, possibly due

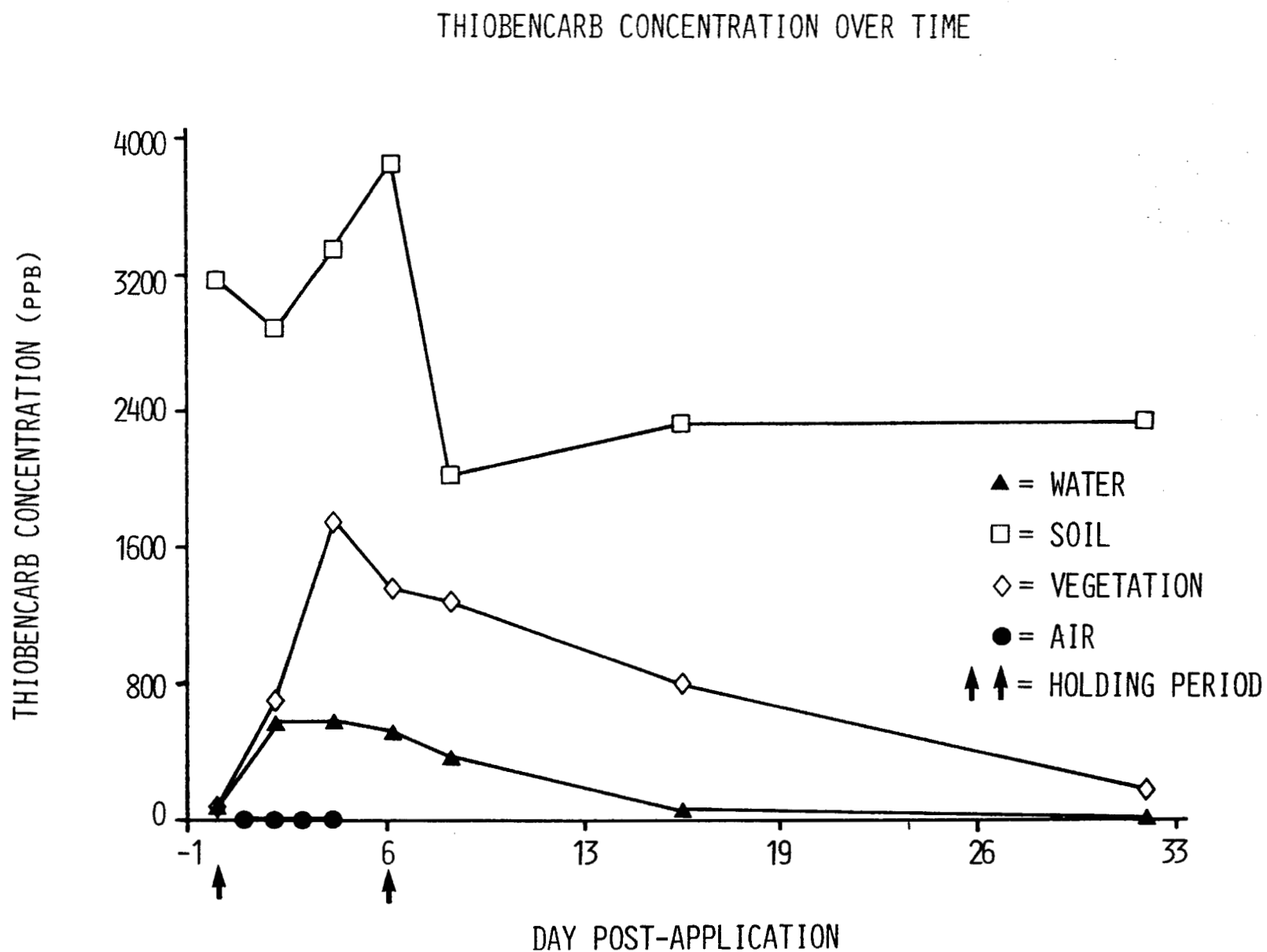


FIGURE 9. CONCENTRATION OF THIOBENCARB IN WATER, SOIL, VEGETATION AND AIR. EACH POINT IS A MEAN OF 16 SAMPLES COLLECTED FROM MASS BALANCE FIELD #3.

THIOBENCARB PHASE PARTITION COEFFICIENTS

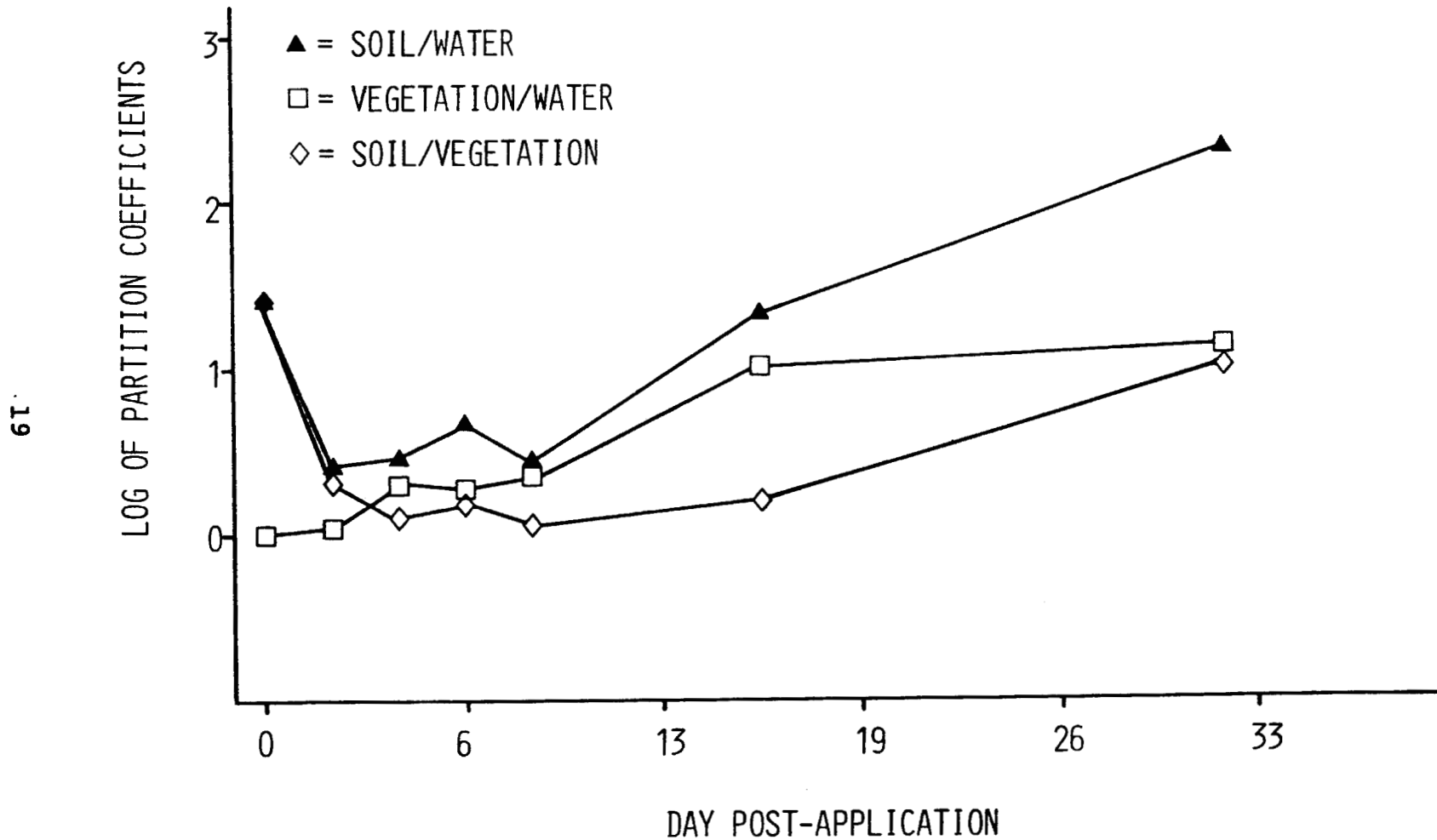


FIGURE 10. EACH THIOBENCARB PHASE PARTITION COEFFICIENT IS A RATIO OF THE VALUES DEPICTED IN FIG. 9.

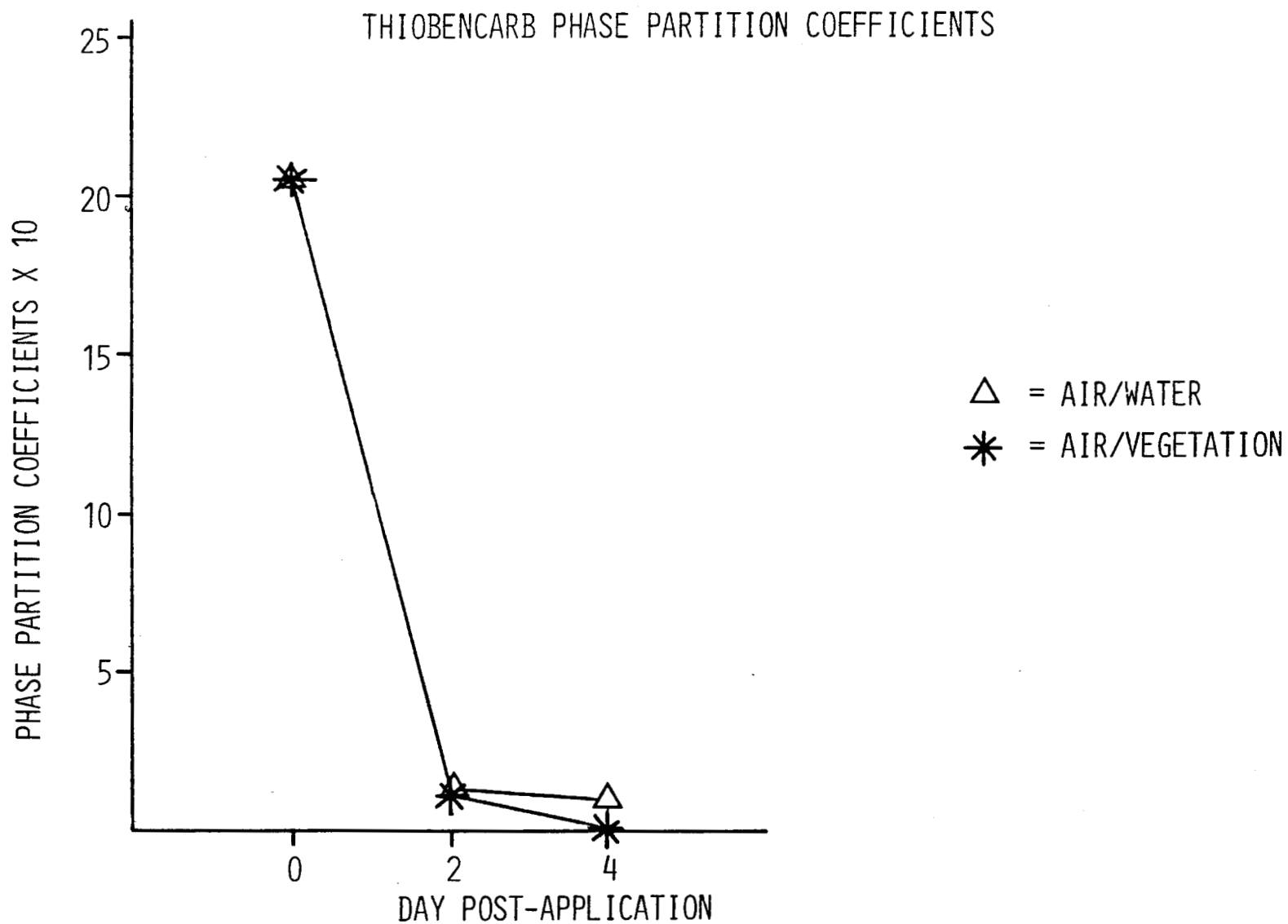


FIGURE 11. EACH THIOBENCARB PHASE PARTITION COEFFICIENT IS A RATIO OF THE VALUES DEPICTED IN FIGURE 9.

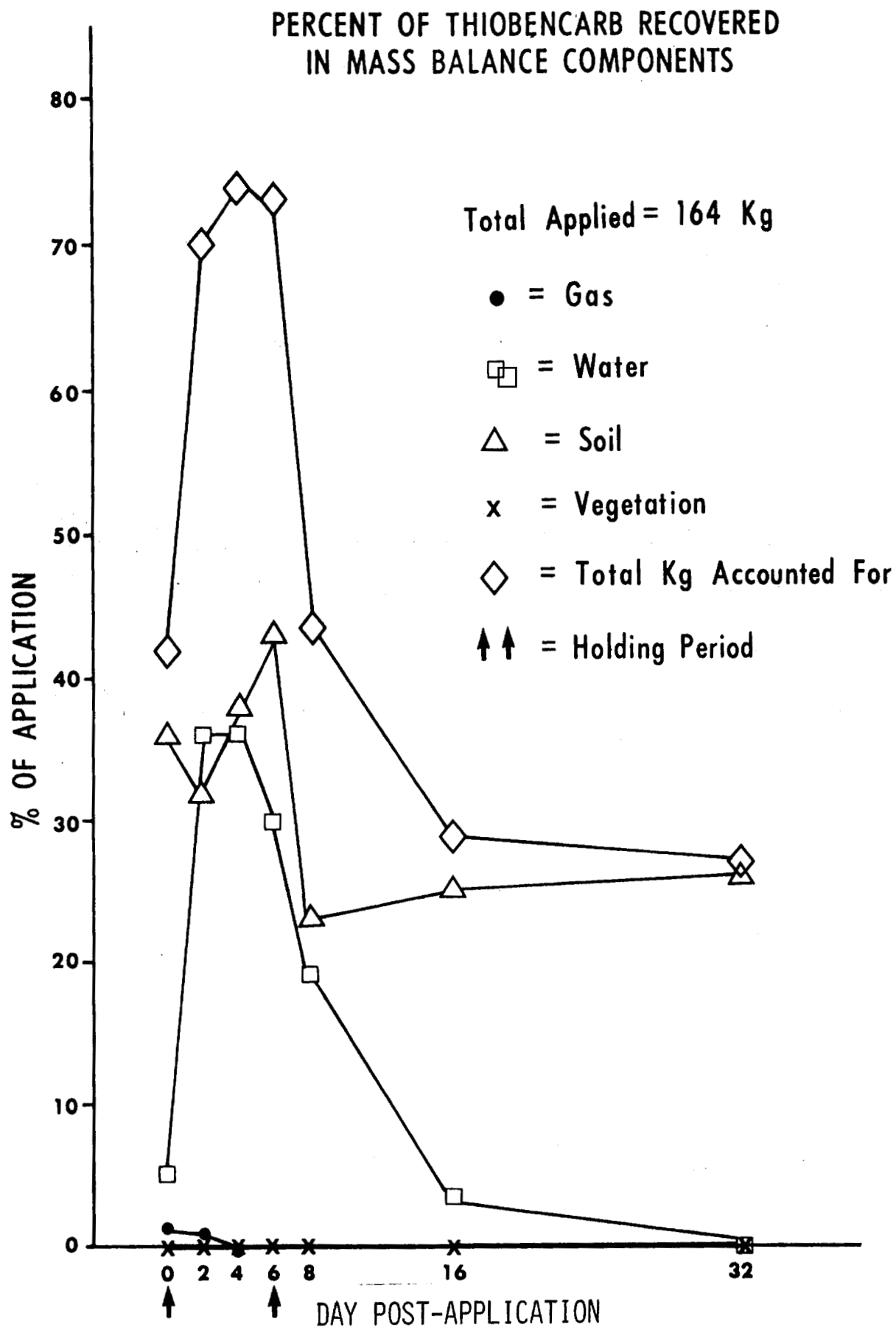


Figure 12. Mass balance budget of thioencarb. The total applied was calculated from herbicide deposition samples. After day 6, water was released from the rice field causing a dramatic decline in the water component and the total kg accounted for.

to an inefficient soil collection technique which was modified during subsequent sampling. The soil component contained the largest amount of thiobencarb (36, 32, 38 and 43% on days 0, 2, 4 and 6, respectively), followed by water (5, 37, 37 and 30% on days 0, 2, 4 and 6, respectively), air (1.0, 0.85 and 0.05% on days 0, 2 and 4, respectively) then vegetation (less than 0.05% on all days). The total amount accounted for beyond day 6 declined dramatically because of release of flood water from the field. However, the total amount for days 16 and 32 remained about the same (29 and 27%, respectively) due to the retention of thiobencarb in soil.

The ANOVA results are presented in Table 3. There were no significant differences in thiobencarb concentrations among sites in water, soil or vegetation. There was no significant difference in sulfoxide concentration in water among sites. Sulfoxide was not analyzed for in soil because it could not be effectively isolated (extraction efficiency was less than 20%). Sulfoxide concentrations were all below the MDL in vegetation (MDL = 500 ppb), therefore no statistical analysis was conducted. Since there were no significant site effects, the 4 sites were averaged to get a mean paddy concentration and the ANOVA was run again. By averaging the 4 sites, the problem of large variability in site observations obscuring paddy and day effects is removed and the new ANOVA design is:

Source of Variation	Degrees of Freedom
Paddy	3
Day	6
Error	18
Total	27

Results from these ANOVA's are presented in Tables 4 and 5.

The ANOVA concerning the water component (Table 4) indicated a significant difference in thiobencarb concentrations among paddies. Duncan's Multiple Range test (DMRT) indicated paddy one had a significantly higher concentration of thiobencarb than paddy 4. This difference was attributed to the side dressing of paddy one. (Often, weed growth was particularly thick along the edge of a field. These areas got extra herbicide dressing to combat that problem.) There was also a significant difference in thiobencarb concentrations among days post-application. The DMRT for days post-application showed that days 2, 4 and 6 had higher concentrations than all other days. Day 8 declined some, followed by 16, 32 and 0 (the lowest concentrations) lumped into a third category. The low concentration of thiobencarb on day 0 is indicative of its low solubility in water. The t-test for 2 vs 6 days post-application was not significant indicating that thiobencarb concentrations did not significantly decline during the 6 day holding period. The t-test for 8 vs 32 days post-application was significant, indicating that thiobencarb concentrations in water were declining. This was expected since

Table 3. Analysis of Variance Results for Thiobencarb and Its Sulfoxide Breakdown Product.

Source of Variation	df	Thiobencarb			Sulfoxide
		<u>Water</u>	<u>Soil</u>	<u>Vegetation</u>	<u>Water</u>
		F-test	F-test	F-test	F-test
Paddy	3	3.78*	2.23	1.70	1.04
Day	6	34.25**	1.10	2.81*	15.83**
Error	18				
Site	3	0.92	0.54	1.22	1.43
Site x Day	18	0.92	1.12	0.58	0.71
Site x Paddy	9	0.89	4.97	0.83	1.28
Error	54				

* = Significant at the 5% level.

**= Significant at the 1% level.

The sulfoxide degradation product was not analyzed for in soil. An ANOVA was not conducted on the concentration of sulfoxide in vegetation because all were below the minimum detectable level.

Table 4. Statistical Analyses of Thiobencarb and Sulfoxide Concentrations in Water.

<u>ANOVA Results</u>		<u>Thiobencarb</u>	<u>Sulfoxide</u>
<u>Source of Variation</u>	<u>df</u>	<u>F-test</u>	<u>F-test</u>
Paddy	3	3.76*	1.09
Day	6	34.18**	15.82**

DUNCAN'S Multiple Range Test

<u>Paddy #</u>	<u>Mean Thiobencarb Concentration (n=7)</u>	<u>Mean Sulfoxide Concentration (n=7)</u>
1	388 Y	33
2	300 Y Z	26
3	318 Y Z	34
4	233 Z	26
<u>Day Post Application</u>	<u>(n=4)</u>	<u>(n=4)</u>
0	79 C	3 G
2	568 A	34 E F
4	576 A	57 D
6	515 A	49 D E
8	367 B	45 D E
16	56 C	18 F G
32	8 C	3 G

Means followed by the same letter are not significantly different at the 5% level. Sulfoxide concentration among paddies was not significant, therefore DMRT was not run.

t-test

	<u>Thiobencarb</u>		<u>Sulfoxide</u>	
	2 vs 6 days	8 vs 32 days	2 vs 6 days	8 vs 32 days
t' =	0.98	11.22***	1.97	9.11***

* = Significant at the 5% level.

** = Significant at the 1% level.

*** = Significant at the .1% level.

Table 5. Statistical Analyses of Thiobencarb Concentrations in Soil and Vegetation.

<u>ANOVA Results</u>		<u>Soil</u>	<u>Vegetation</u>
<u>Source of Variation</u>	<u>df</u>	<u>F-test</u>	<u>F-test</u>
Paddy	3	2.23	1.70
Day	6	1.10	2.81*
Error	18		

DUNCAN'S Multiple Range Test

<u>Day Post Application</u>	<u>Mean Thiobencarb Concentration (n=4)</u>	
	<u>Soil</u>	<u>Vegetation</u>
0	3171	78 Z
2	2883	691 X Y Z
4	3351	1754 X
6	3858	1358 X Y
8	2023	1283 X Y Z
16	2195	797 X Y Z
32	2329	169 Y Z

Means followed by the same letter are not significantly different at the 5% level.

<u>t-test</u>	<u>Soil</u>		<u>Vegetation</u>	
	2 vs 6 days	8 vs 32 days	2 vs 6 days	8 vs 32 days
t' =	.869	.301	1.412	2.725*

* = Significant at the 5% level.

thiobencarb-laden water on the field was being diluted with uncontaminated water flowing onto the field. In the ANOVA for sulfoxide concentrations in water, a significant difference was indicated among days. The DMRT for days showed a similar pattern to thiobencarb, just lagging behind a few days. The t-test results were the same as for thiobencarb, not significant during the holding period yet a significant decline afterwards.

Background thiobencarb and sulfoxide water concentrations were all below the MDL (3 ppb), as were all inlet samples. A DMRT including day -1, (results not shown) indicated that day -1 was not significantly different from days 0, 16 and 32 in thiobencarb concentration. For sulfoxide concentration, day -1 was not significantly different from days 0 and 32. Therefore, after 32 days, the concentrations of thiobencarb and sulfoxide in water returned to pre-application levels.

The ANOVA for soil (Table 5) indicated no difference in thiobencarb concentrations among paddies or days. This indicated that thiobencarb soil concentrations were not significantly different across the field and did not decline within 32 days. The t-tests confirmed the ANOVA results, neither one being significant.

A separate ANOVA, (results not shown), using background soil concentrations indicated a significant difference among days. The DMRT showed that background concentrations (below the MDL of 100 ppb) were significantly less than post-application concentrations. Since water flowing into this field did not contain a detectable concentration of thiobencarb and background levels for soil and water were all below the MDL, the concentrations reported throughout the entire month are the result of the herbicide application on May 30, 1983.

The ANOVA of vegetation (Table 5) indicated a significant difference among days but not among paddies. In the DMRT the vegetation concentration of thiobencarb on days 4 and 6 was significantly higher than on day 0. (The mean thiobencarb concentration reached a peak near day 4.) This indicates a lag time between thiobencarb application and plant uptake. The concentration of 78 ppb on day 0 might not actually reflect thiobencarb incorporated into vegetation. Of the 16 samples taken that day, only two contained thiobencarb. One sample had 1100 ppb, the other, 150 ppb. All the rest (14 samples) were less than the MDL (50 ppb for samples ≥ 40 ug). The vegetation samples were rinsed twice, once before leaving the field and again when brought into the laboratory. Perhaps these two samples were not thoroughly washed, either in the field (which would enable the uptake of thiobencarb in transit) or in the lab. In the t-tests, vegetation concentrations at 2 vs 6 days post-application were not significantly different whereas for 8 vs 32, there was a significant decline.

FLOW FIELDS

Results of flow field monitoring are depicted in Figures 13 through 17. From these graphs it appears that most fields had a markedly different drain flow pattern. Fields 9 and 10 were the only similar ones, with flows about 6l l/sec at the end of the holding period, a dip to 1-3 l/sec, followed by a flow between 10 and 40 l/sec for over a month of sampling. On July 15, drain flow rates of both fields tapered off below 1 l/sec. These fields were side by side, owned and managed by the same grower, and seeded and sprayed at the same time. The three other fields (7, 13 and 14) did not have an obvious pattern.

The erratic drain flow patterns were to be expected since flow was not governed by a physical process but by each individual growers' management scheme.

Concentration of thiobencarb at drains showed a general decline over time for all flow fields. Samples taken soon after thiobencarb application (within 24 h) frequently did not have the highest concentration. Peak values occurred 1-6 days post-application and ranged from 233 (field 13) to 1260 ppb (field 9). Generally, the concentration of thiobencarb in water did not drop below 100 ppb before 12 days or below the MDL before 27 days post-application.

Flux values varied with concentration and/or flow, depending on the magnitude of those values. When drain flow rates were erratic (as in fields 7, 13 and 14) so were flux values. In fields 9 and 10, where drain flows were fairly uniform, flux curves were similar to concentration curves.

Due to the erratic pattern of flux values in 3 of 5 fields, an equation predicting thiobencarb flux from a "typical" rice field could not be developed. Instead, we attempted to predict thiobencarb concentrations at the drain of a "typical" rice field. The independent variables used to predict thiobencarb concentrations were the same as those mentioned in the methods section.

The volume of water standing on a field varied from 5.7×10^6 to 7.6×10^7 l, depending on field size and water depth. Net flow was usually a negative rate, i.e. more water flowing into a field than off a field. Evaporation, transpiration and grower manipulation of inflow and outflow were largely responsible for that condition.

Results of the stepwise linear regressions run on individual fields are shown in Table 6. Day 0 was omitted from all regression analyses because concentrations collected then were always lower than those from subsequent samples. This factor would cause a sharp inflection point in the concentration curve, making a simple linear equation inadequate for predictive

Bolero Field #7

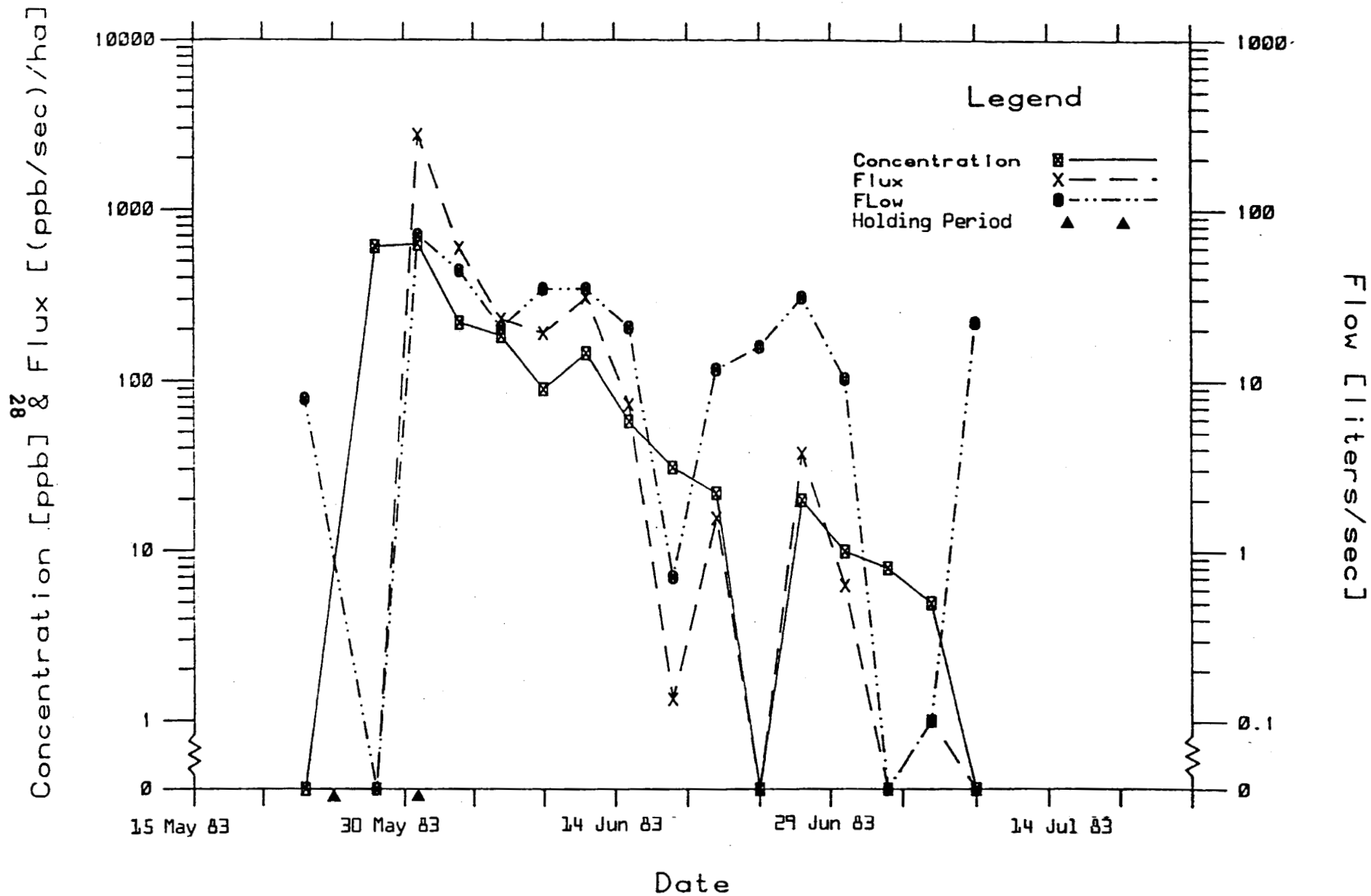


Figure 13. Thiobencarb flow field #7. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Bolero Field #9

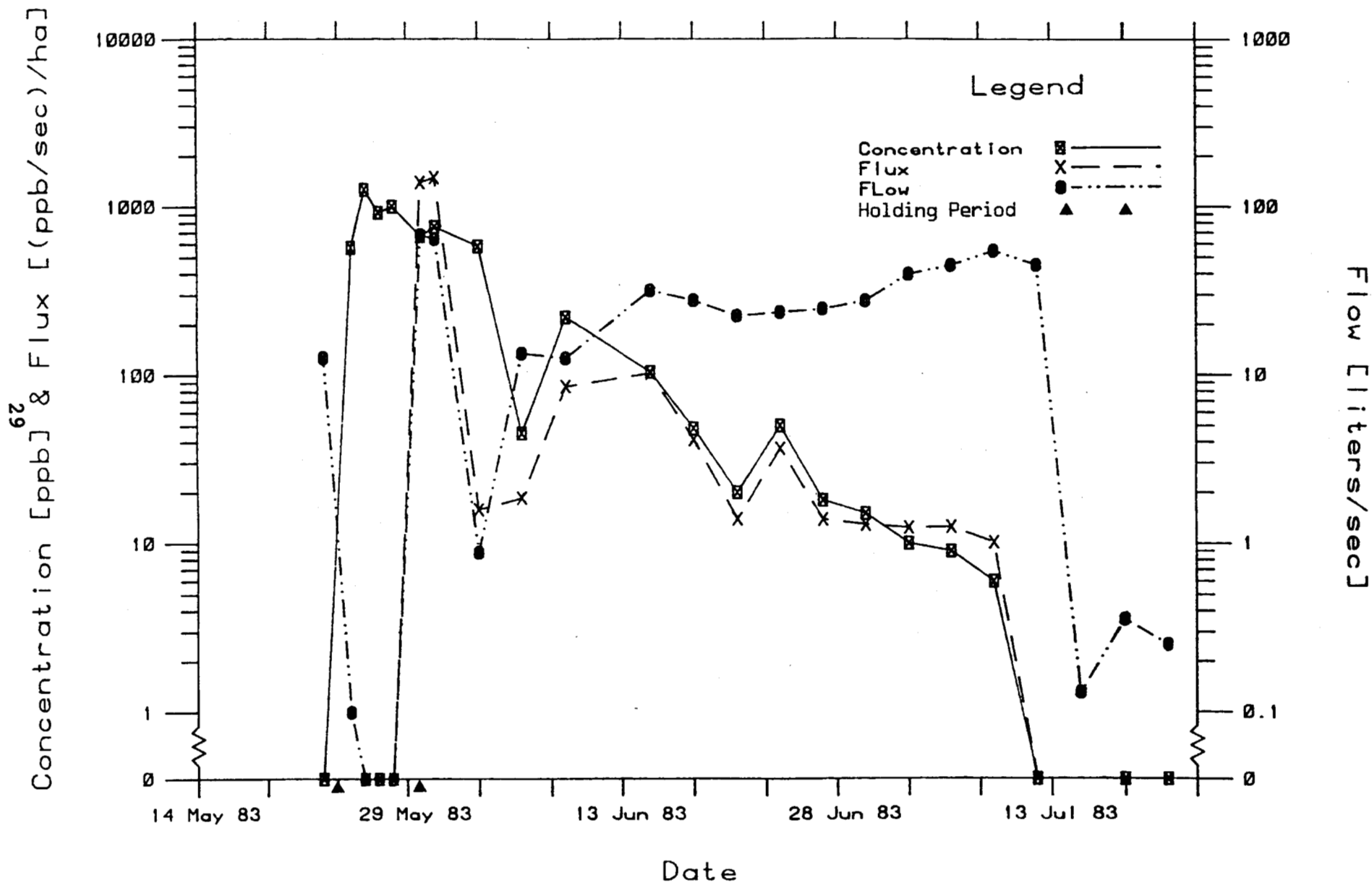


Figure 14. Thiobencarb flow field #9. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Bolero Field #10

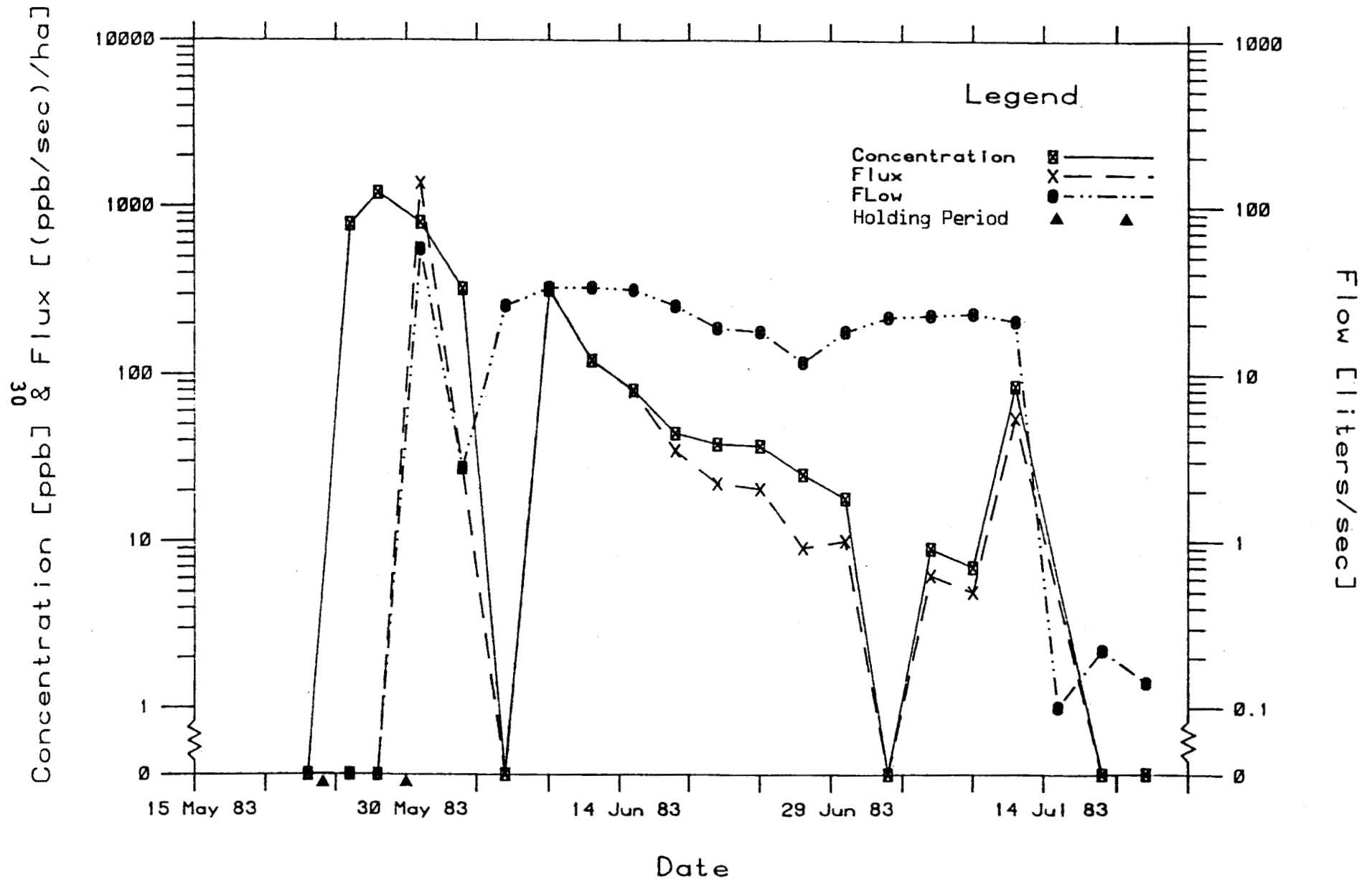


Figure 15. Thiobencarb flow field #10. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Bolero Field #13

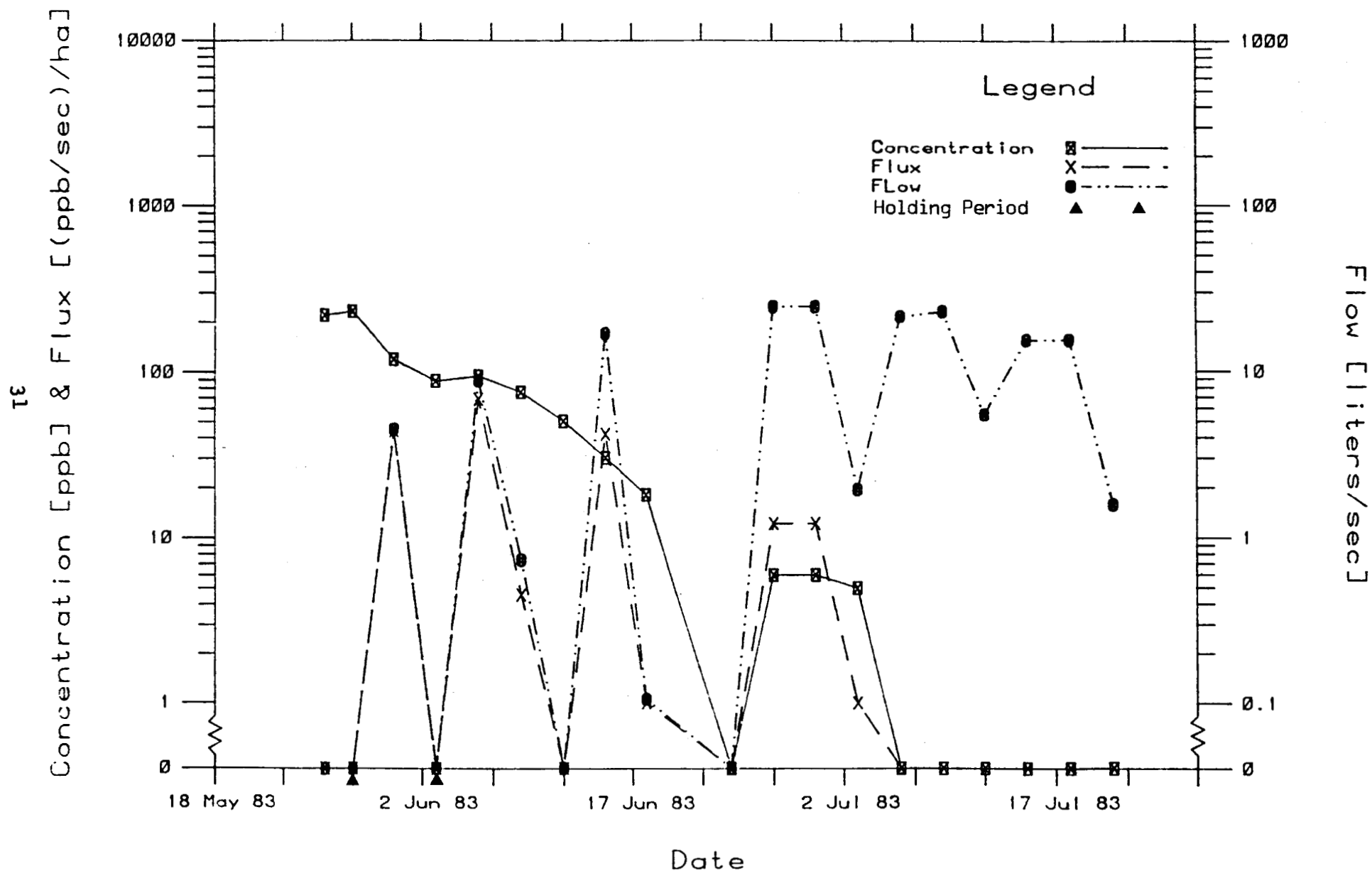


Figure 16. Thiobencarb flow field #13. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Bolero Field #14

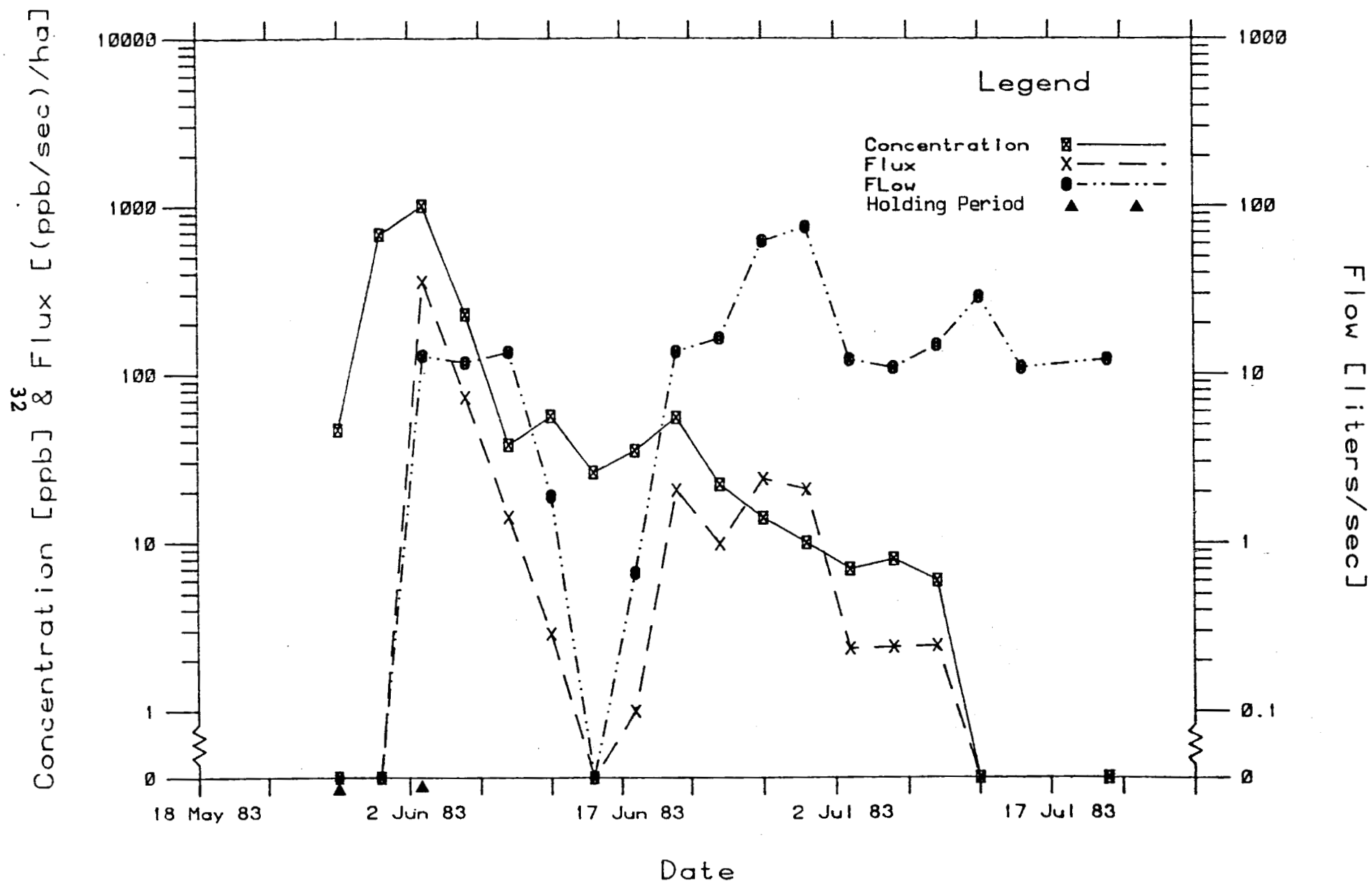


Figure 17. Thiobencarb flow field #14. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) in on the right y-axis. Arrows on the x-axis indicate the holding period.

Table 6. Thiobencarb Flow Field Regression Equations

Field #	Equation ^{a/}	SEE ^{b/}	SEC ^{c/}	R ² ^{d/}
7	y = 949 - (618)(log day + 1)	87	75	.84
9	y = 1299 - (799)(log day + 1)	188	93	.79
10	y = 1309 - (812)(log day + 1)	180	117	.74
13	y = 220 - (143)(log day + 1)	11	7	.98
14	y = 1089 - (710)(log day + 1)	183	148	.62
All	y = 1122 - (731)(log day + 1)	166	83	.73

a/ The estimate y = the concentration of thiobencarb in ppb.

b/ SEE = Standard error of the estimate.

c/ SEC = Standard error of the coefficient.

d/ R² is the proportion of the variance of the dependent variable explained by the regression equation.

purposes. All fields had very similar (best) regression equations with the log of day post-application being the sole variable entered into the best fit regression equation. Approximate 95% confidence limits about the log of day coefficients in all equations (except field 13) overlapped. (These 95% confidence limits were calculated by adding and subtracting twice the SEE to the respective coefficient.) Field 13 was smallest of all fields and had the lowest concentrations, which may have contributed to the exceptionally good regression results ($R^2 = .98$ and $SEE = 11$). Since these equations were fairly similar, all 5 fields were combined to generate one equation describing the concentrations of thiobencarb at field drains.

Concentration, drain flow, volume and net flow were averaged by day among fields. These averages were then entered into the regression program and the final equation is shown in Table 6. Figure 18 depicts the observed and predicted concentrations over time. The observed concentrations do not smoothly decline with time, therefore our equation does not fit the observed values precisely. However, the predictive equation does bring out the general decline in thiobencarb concentration over time.

Mass discharge of thiobencarb from flow fields was also calculated. To determine the amount of thiobencarb leaving a field, flow rates were multiplied by drain concentrations, then extrapolated over a 24-hour period. This daily value is merely a rough estimate of thiobencarb mass discharge. Table 7 contains a summary of this information. Mass discharge for the month following thiobencarb application ranged from 0.5 to 32 kg. The amount discharged in 1 month ranged from 1 to 28% of the total applied. Beyond 1 month, weekly mass discharge values were well below 1% of the total amount applied.

THIOBENCARB CONCENTRATION AT DRAIN,
PREDICTED AND OBSERVED VALUES.

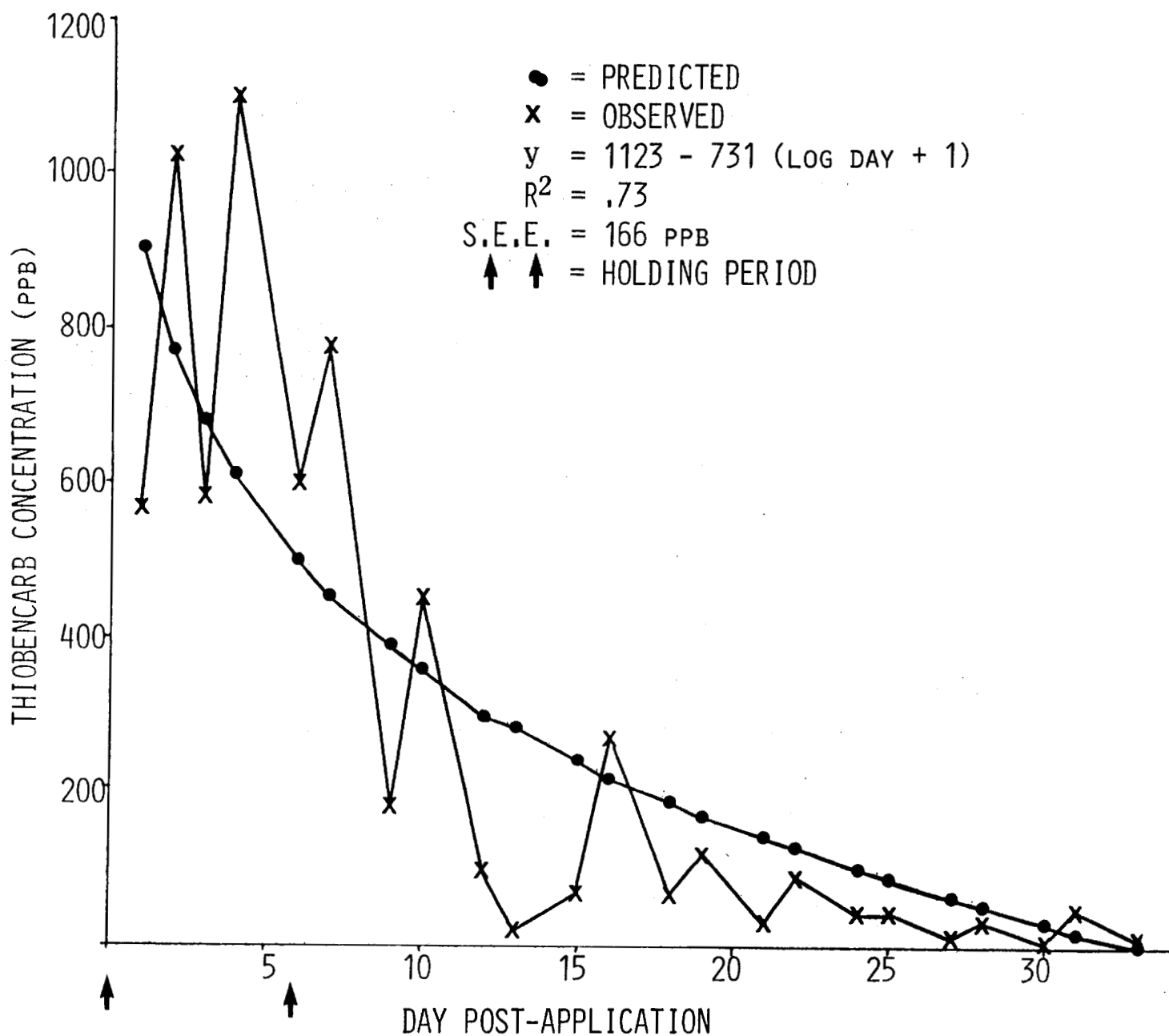


FIGURE 18. OBSERVED (x) AND PREDICTED (●) THIOBENCARB CONCENTRATIONS AT THE DRAIN OF FLOW FIELDS. OBSERVED CONCENTRATIONS WERE AVERAGED AMONG FIELDS (N = 2 TO 4) BY DAY. S.E.E. = STANDARD ERROR OF THE ESTIMATE (y).

Table 7. Thiobencarb Mass Discharge from Flow Fields.

Field #	Kg Applied	Amount of Thiobencarb Discharged (kg)	Theoretical Discharge for 4 Weeks (kg)	% of Applied
7	73	5.88 (8) ^{a/}	20.58 ^{b/}	28 ^{c/}
9	144	9.18 (8)	32.14	22
10	144	6.95 (8)	24.33	17
13	54	0.17 (9)	0.52	1
14	162	1.58 (9)	4.92	3

^{a/} Numbers in parentheses = the number of days summed into the amount of Thiobencarb discharged.

^{b/} Values in this column were calculated by multiplying the mean amount of Thiobencarb discharged by 28 (the number of days in 4 weeks).

^{c/} Percentages in this column = theoretical discharge for 4 weeks divided by total Kg applied.

DISCUSSION

From the mass balance segment of this study it appears that thiobencarb is a stable compound in soil and water. The ANOVA's indicate there is no significant decline in soil concentrations even up to 32 days after application. The concentration of thiobencarb in water does not decline significantly during the 6 day holding period. Water concentration declines only after the release of flood water. Studies by Chevron Chemical Company indicate that even holding water up to 10 days post-application does not reduce thiobencarb concentration in water (15). Sulfoxide was found over the course of the month, but was not more than 10% of thiobencarb concentrations. Even though thiobencarb is not especially soluble (30 mg/l at 20°C), the material that does dissolve tends to remain.

There is some repartitioning of thiobencarb from soil back into water as indicated by the mass discharge figures calculated from flow fields. Yet, of the 8 or 9 days sampled from flow fields during 1 month, the first 2 samples (taken 6-9 days post-application) account for 73% of the total amount of thiobencarb discharged from a field. This implies that most of the thiobencarb flowing from a field comes off with the holding-period water. Comparatively smaller amounts are discharged during the remainder of the month, this perhaps being repartitioned from soil back into water and/or from water residuals left on a field.

Thiobencarb is not very volatile from water. Henry's Law constant = 1.6×10^{-9} atm.m³/mole (a vapor pressure/water solubility ratio). The percent of thiobencarb lost to air was low when compared with the total amount of herbicide applied but examination of this with respect to the amount in water available for volatilization would be more accurate. The maximum concentration of thiobencarb in air reported by Dr. Seiber was .16 ppb on the day of application. In terms of the total amount of thiobencarb applied, the % evaporating was 1.3, but based on the amount in water, it was 24.5. At 2 days post-application these values were 0.9 and 2.5%, respectively. The large drop in % from 0 to 2 days post-application may be due to; the low solubility of thiobencarb in water so that the amount of thiobencarb in water on the day of application was lowest of all holding period days and, the higher flux on 0 vs 2 days post-application. This flux differential may be due to; 1. aerial contamination in the vicinity of the air samplers, 2. volatilization of thiobencarb from impaction on solid surfaces e.g. ditch banks, 3. volatilization from floating thiobencarb slicks in the water surface and/or, 4. water-air partitioning.

The concentration of thiobencarb in vegetation increases rapidly during the holding period and declines slowly

afterwards. Rice and barnyard grass are in the 1-2 leaf growth stage when thiobencarb is applied, a time of rapid growth for young seedlings. During this period, plants are taking in large amounts of water and nutrients to sustain growth. With this water, thiobencarb is also taken up through roots, stems and leaves of adult rice and weed plants and mesocotyl, coleoptile and seeds of immature plants (16). From the vegetation/water phase partition coefficients it is seen that plants contain 1-3 times the concentration found in water. There is a gradual increase in the coefficients through day 8 indicating that the longer plants sit in water containing thiobencarb, the more they will take up. Other research confirms this observation (17). Once thiobencarb-laden water is released and the field is refilled with uncontaminated water, the vegetation/water coefficients increase dramatically. This increase indicates that as the water concentration drops off, the concentration in vegetation remains comparatively high. At 32 days post-application, there was 169 ppb thiobencarb in vegetation (which includes weeds and rice). If thiobencarb remains in soil, and is slowly repartitioned into water over time, one would suspect it will continue to be transferred to rice and may be present when harvested. Even though thiobencarb may degrade ultimately to CO_2 in young plants (18), there are growth stages in the rice life cycle where most nutrients are taken up and shunted into grain production (roughly 100 to 140 days after sowing (4)). Perhaps at these times, thiobencarb gets incorporated into grain without being degraded. One study found 300 ppb of thiobencarb in harvested grain (17).

The components air, water, vegetation and soil, when examined in a mass balance budget, indicate that soil contains and retains the highest thiobencarb concentration. The water component is also high during the holding period but declines to 8 ppb 32 days post-application once uncontaminated water replaces holding-period water. The evaporative component is small in comparison with soil and water and contributes very little to the mass balance budget. However, it is important to examine the volatilization of thiobencarb with respect to water, the medium from which it volatilizes (as shown above).

Of particular interest is the relatively low contribution of vegetative thiobencarb to the mass balance budget. This was unexpected since vegetation is the target organism, and rice, as well as barnyard grass, takes up thiobencarb readily (15). Perhaps the difference in these components lies in their relative volumes and not in concentrations. Water typically had the largest volume, which varied by day (depending on the water management strategy). Soil volume remained the same since samples were always collected 4 in deep. Vegetation had the lowest volume even after the rice plants matured so its contribution to the total mass balance budget was small. In addition, vegetation samples contained broad leaved plants and other weeds as well as rice. Thiobencarb is not effective at controlling broad leaved weeds and therefore the presence of

these may have diluted the vegetation contribution to the mass balance budget.

To be able to predict the flux of thiobencarb into drainage canals requires a predictable water flow or water management scheme. Unfortunately, because of wind, invertebrate pests, weed infestation and algae growth, drain flows vary widely and sporadically. Therefore, instead of using flux, an attempt was made to describe the change in thiobencarb concentrations (at field drains) over time. This too varied quite markedly, with an overriding inverse relationship between concentration and time. Our descriptive equation depicts this trend but the R^2 (.73) value indicates a mediocre fit of the data.

Part of the problem in using a simple linear regression to predict thiobencarb dumping into drainage canals lies in the fact that we are dealing with two different field processes. Water was held on a field for 6 days and from Figure 18, it appears that during that time there was no relationship between time and concentration (slope = 0, i.e. no change in concentration with time). The spikes in this portion of the curve may be related to sampling design (see below) and/or chemical analysis error. Once water is released from a field (after day 6), a decline in concentration occurs with time. The spikes in this portion of the curve may reflect the repartitioning of thiobencarb from soil into water, over-spray from adjacent fields or variability associated with sampling design or chemical analysis.

Another problem arises from the taking of point samples in time. On any one sample date, from 2 to four fields were averaged into one observation. However, each sample was an instantaneous, grab sample. We don't know what the variation is from replicate samples taken over the course of a few hours from a single drain. Since we only specified the day each field was to be sampled, the hour of sampling was at random (during daylight hours). The spikes in our observed curve may reflect this variation. Another source of variability is the use of different sized fields managed by different growers. However, one is never going to be able to predict thiobencarb discharge from fields to drainage canals and canals to rivers unless all contributors are considered. For these reasons only a very general equation can be developed, reflecting high thiobencarb concentrations released immediately following the holding period with a gradual decline over time as the thiobencarb-laden water becomes diluted and flushed from the field.

The most striking result of this study is the persistence of thiobencarb in soil and water. Sixty-one % of the peak soil concentrations and 10% of peak vegetation concentrations are still present 1 month after application. In comparison, little thiobencarb is found in water at the end of the month because of dilution and mass flow of herbicide-laden water off the rice field. However, when paddy water is held 6 days after application, 91% of peak concentration still remains on the field

demonstrating the stability of this compound in water. About 27% of the total applied thiobencarb remains on the field after 1 month, most of which is in soil. It is clear that thiobencarb is quite stable in water and soil and lingers much longer than is necessary to complete its function. Further, since it persists in the field, rice plants have opportunity to take it up and possibly incorporate it into grain.

Part II. Molinate

Materials and Methods

The environmental assessment of molinate mass balance and flow dynamics was conducted simultaneously with thiobencarb. The design and mechanics of Part II are similar to that of Part I, detailed in the Materials and Methods section of thiobencarb. There were several minor differences in methodology and these are cited below.

A. Molinate Mass Balance Procedures.

A 101 acre field (Fig. 19), located in Glenn County, was chosen as a site for assessment of the molinate mass balance budget. This field (with a single inlet and drain) was divided into 14 paddies. The first pad, at the site of water inflow, was not seeded and served only as a water warming pad. Sixteen mass balance sample sites were chosen within field #4 using the same criteria described for thiobencarb sample site selection. These sample sites are presented in Figure 19. Ordram 10G (Stauffer) is usually applied by aircraft at the rate of 40 lbs per acre, which contains 10% active ingredient (molinate) and 90% inert ingredients. Applications are usually made when weeds are in early growth stages (spike to 3-leaf stage).

Water flow measurements were made using the same methods described for thiobencarb. Weather data were documented simultaneously for both mass balance fields 3 and 4. Figure 9 indicates the location of weather instrumentation from June 4, 1983 through June 10, 1983. For the remainder of the field study, weather instrumentation was located at Field #3 approximately 100 m north of field #4.

Sampling methodology for water, soil, vegetation, air and mass herbicide deposition followed the same protocol used for the thiobencarb mass balance study, with 2 exceptions. No mass balance sampling was scheduled for 6 days post-application and on day 16 post-application, the test field was drained so a water sample could not be taken.

Field sampling for molinate evaporative flux was performed by personnel from U.C. Davis (see Appendix A for methods). The protocol followed the design used by U.C. Davis for thiobencarb mass balance evaporative flux with some exceptions. High volume air samplers were not incorporated in evaporative flux sampling. Instead, 3 low volume air samplers consisting of a carbon vane

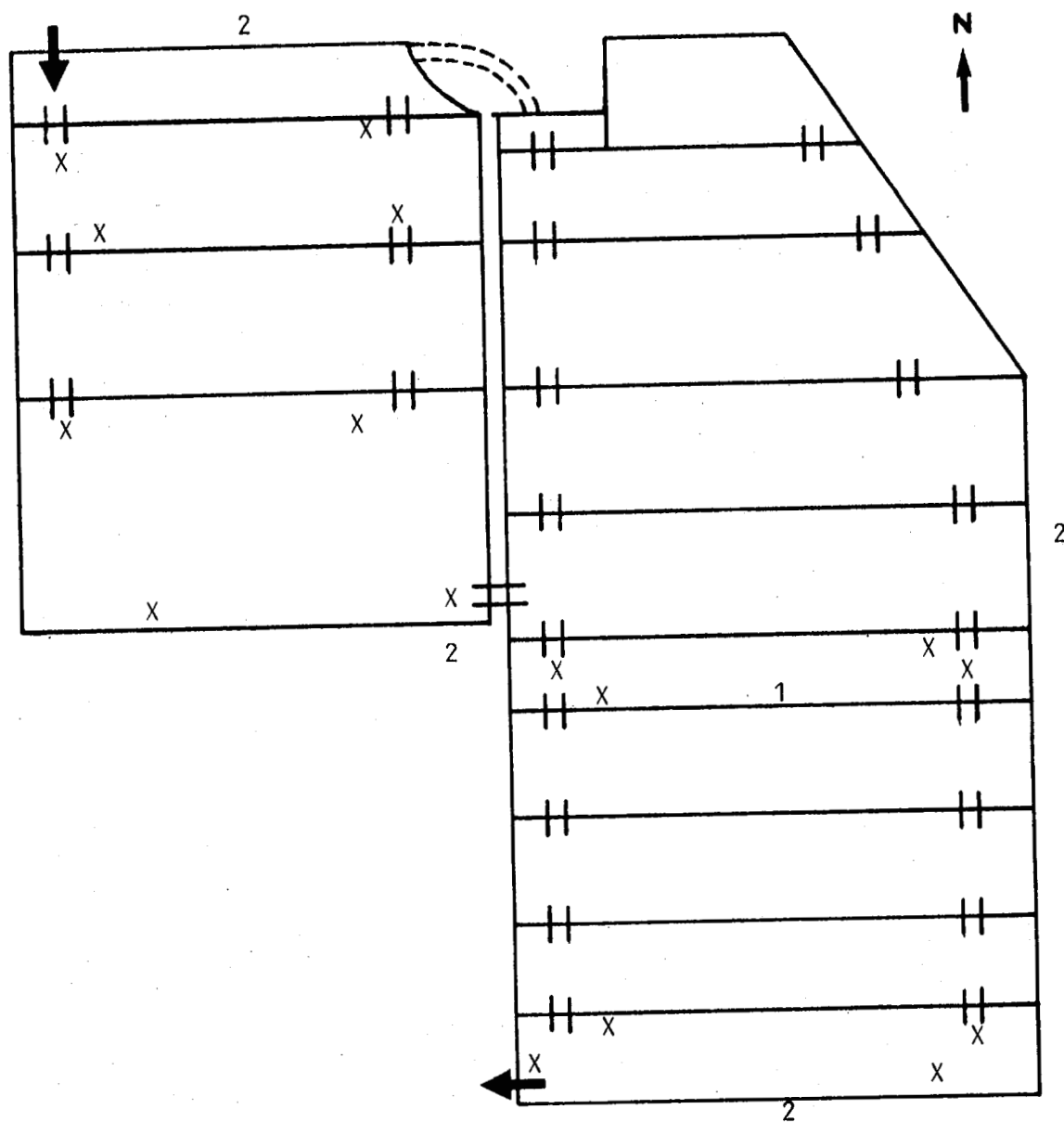


Figure 19. Mass balance field (#4) is 101 acres (42 hectares). Molinate was applied 6/1/83 at 4 lbs AI/A and 6/6/83 at 2.8 lbs AI/A. x= location of the 16 sampling sites. 1 = location of weather instrumentation from 6/4 through 6/10. 2 = location of Hi-volume air samplers.

pump (Gast model 2531) provided a vacuum to draw air at a rate of 21 l/min through single 6 x 5/8 in I.D. glass tubes packed with pre-cleaned XAD-2 macroreticular resin. These 3 tubes were positioned 30, 90 and 190 cm (11.8, 35.4 and 74.8 in) above the rice paddy. The samples were run to establish background levels of molinate from 0730 to 0930 h on June 6. Air samples were then taken during the application from 1645 to 1845 h and immediately following application at 1850 to 2045 h. Samples were taken at 2 h increments from 0700 to 1700 h on days 1, 2 and 3 post-application to establish rates of evaporative flux.

Molinate mass deposition samples were collected on the day of application using the same methodology described for thiobencarb. The application rate was 2.8 lbs active ingredient per acre (AI/A). This was less than the recommended application rate because 4 days prior, an applicaiton of 4 lbs/acre of molinate was made under special circumstances.

All aspects of sample handling including transportation, storage, prioritization and sample security were conducted as outlined for thiobencarb. Samples were analyzed for molinate and the sulfoxide breakdown product of molinate. Chemical analyses followed the protocols outlined in Appendix C.

Statistical analyses were the same as for thiobencarb with a few exceptions. Vegetation was so sparse on days 0, 2 and 4 post-application that only 1 sample per paddy was collected. Therefore, sites were not analyzed for in the ANOVA and the design was the same as for thiobencarb. Samples were not collected 6 days post-application and therefore not included in the ANOVA. However, the background sampling period (day -1) was included in the ANOVA because of the duplicate application of molinate. Finally, t-test comparisons were made between days 0 and 4 (since the holding period for molinate was 4 days) and days 8 and 32. Day 0 was used in the first comparison because of the duplicate application of molinate.

B. Molinate Flow Field Procedures

Nine fields in Glenn and Colusa counties were chosen to assess the concentrations of molinate in the flow of rice paddy water (Figs. 20 through 25). Fields sizes ranged from 40 to 150 acres with an average size of 72 acres. Molinate flow fields were chosen based on the same criteria used for thiobencarb flow fields. All measurements of water flow, sampling methodology, sample handling, security and chemical and statistical analyses followed the protocol described for thiobencarb.

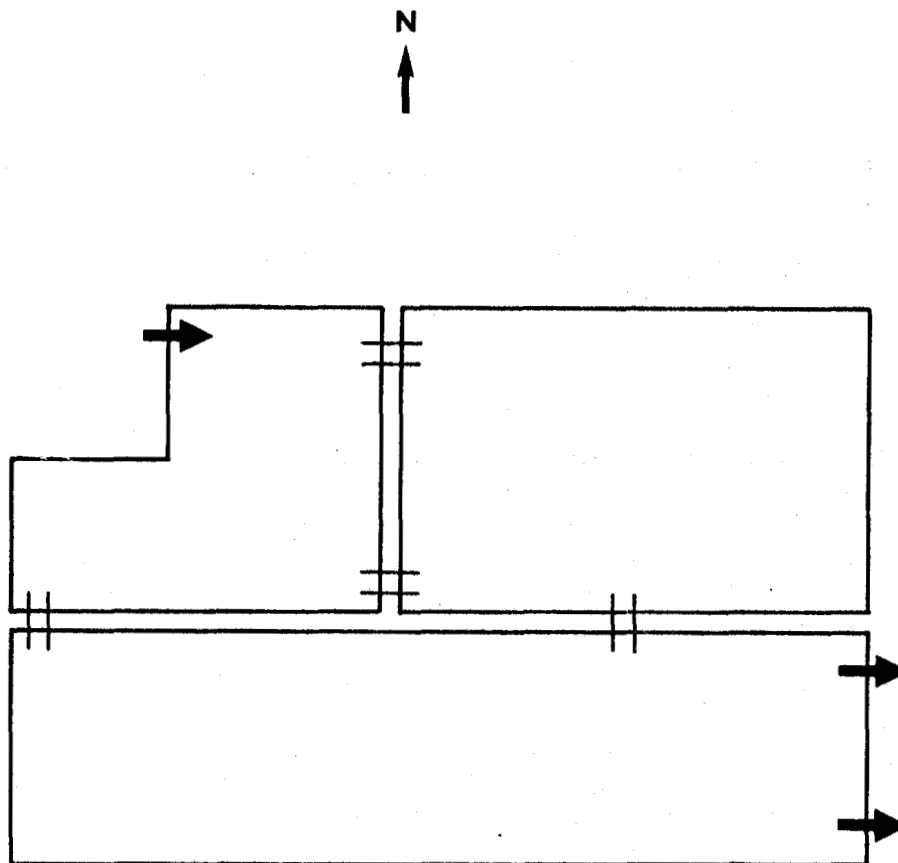


Figure 20. Flow field #1 is 51 acres (21 hectares). Molinate was applied 5/15/83 at 4 lbs AI/A. Arrows indicate field water inlet and outlets.

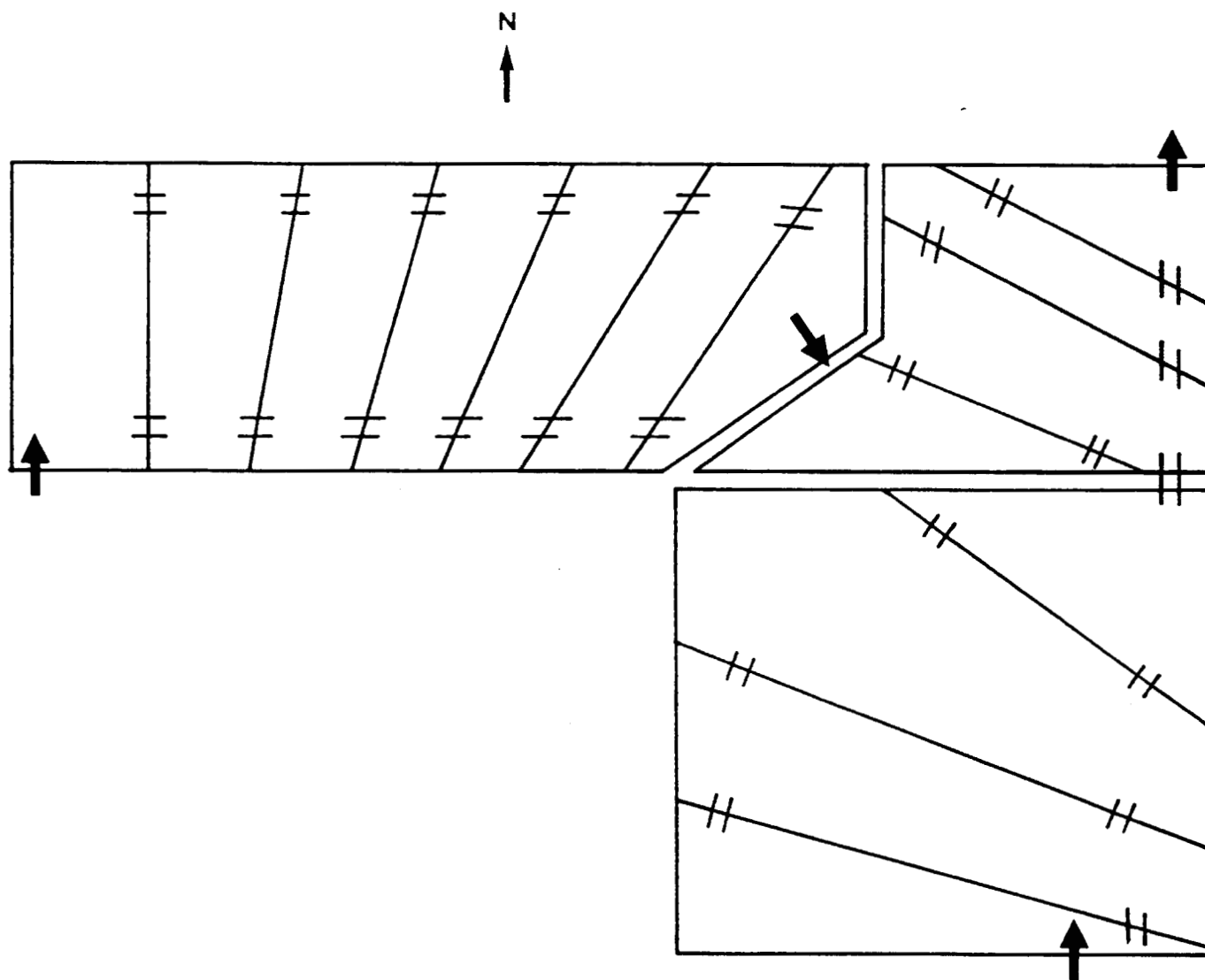


Figure 21. Flow field #6 (top left) and field #5 (right) are 52 acres (22.3 hectares) and 49 acres (20 hectares), respectively. Molinate was applied 5/25/83 at 4 lbs AI/A. Arrows indicate field water inlets and outlets.

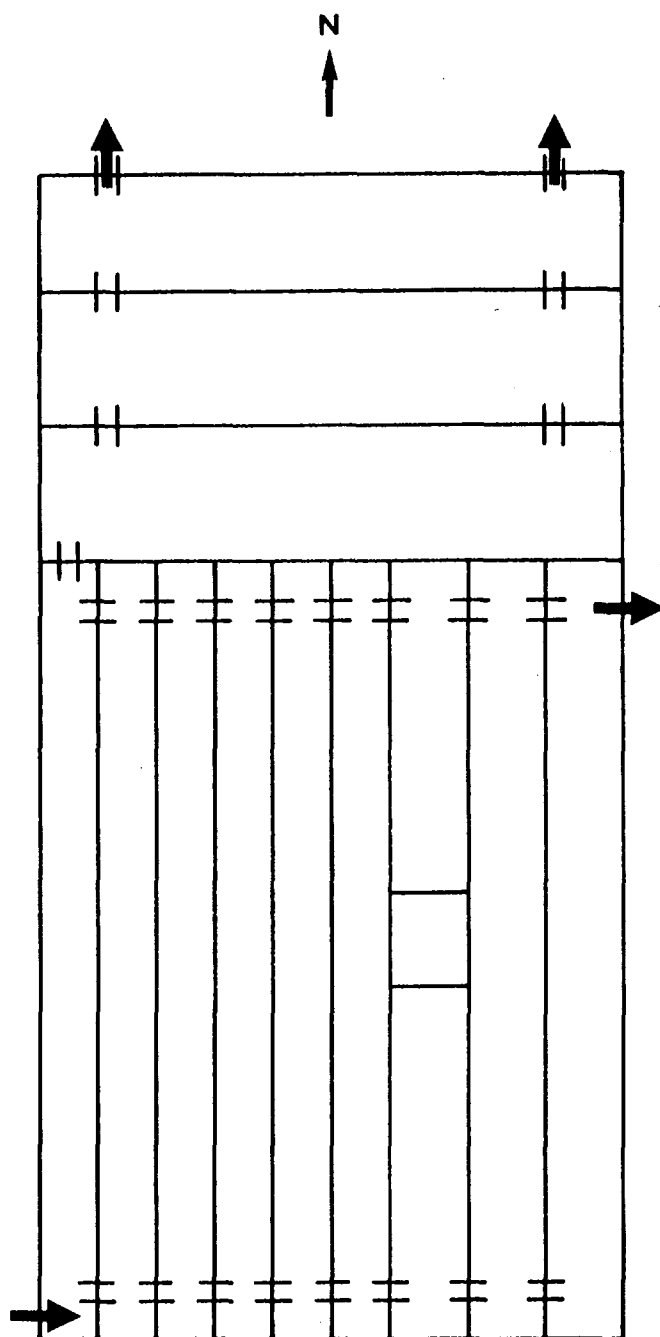


Figure 22. Flow field #8 is 80 acres (32 hectares). Molinate was applied 5/31/83 at 4 lbs AI/A. Arrows indicate field water inlet and outlets.

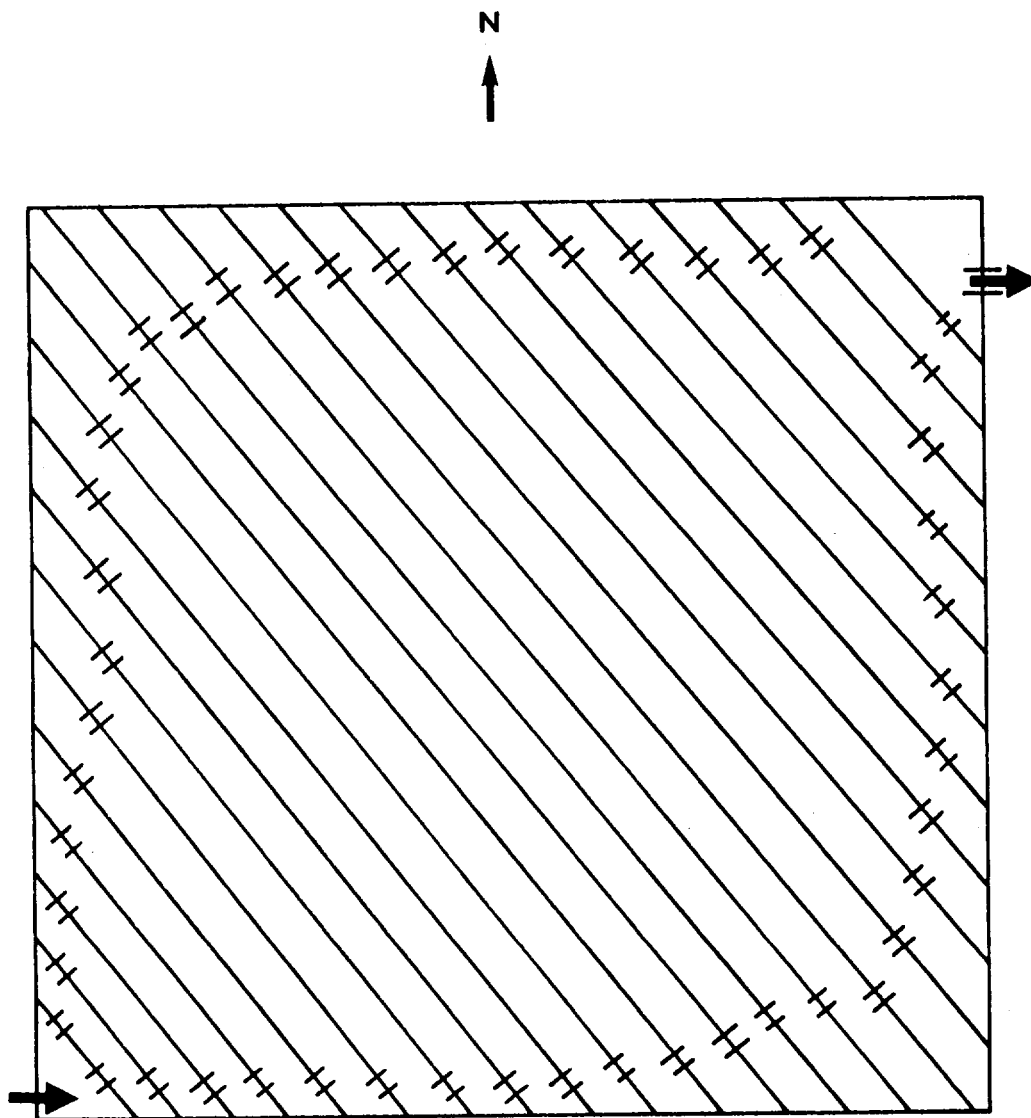


Figure 23. Flow field #11 is 150 acres (61 hectares). Molinate was applied 5/28/83 at 4 lbs AI/A. Arrows indicate field water inlet and outlet.

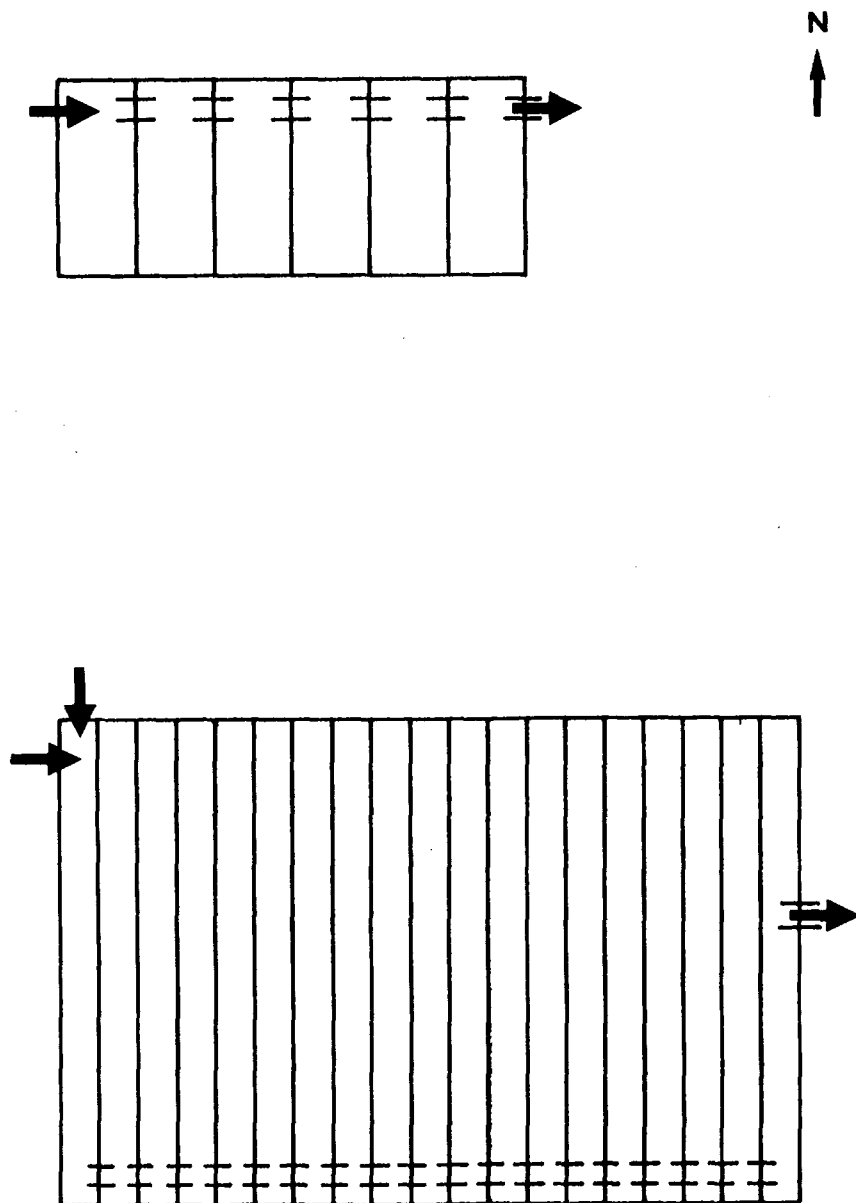


Figure 24. Flow field #12 (top) and field #15 (bottom) are 13 acres (5 hectares) and 56 acres (23 hectares), respectively. Molinate was applied 5/26/83 to field #12 and 6/5/83 to field #15 both at 4 lbs AI/A. Arrows indicate field water inlets and outlets.

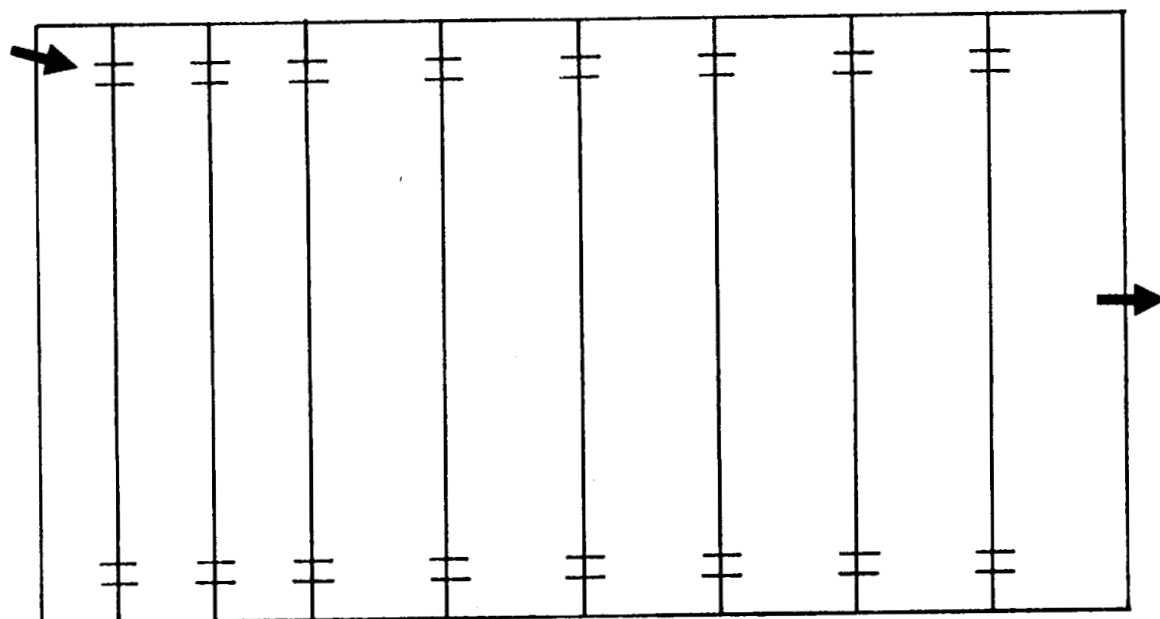
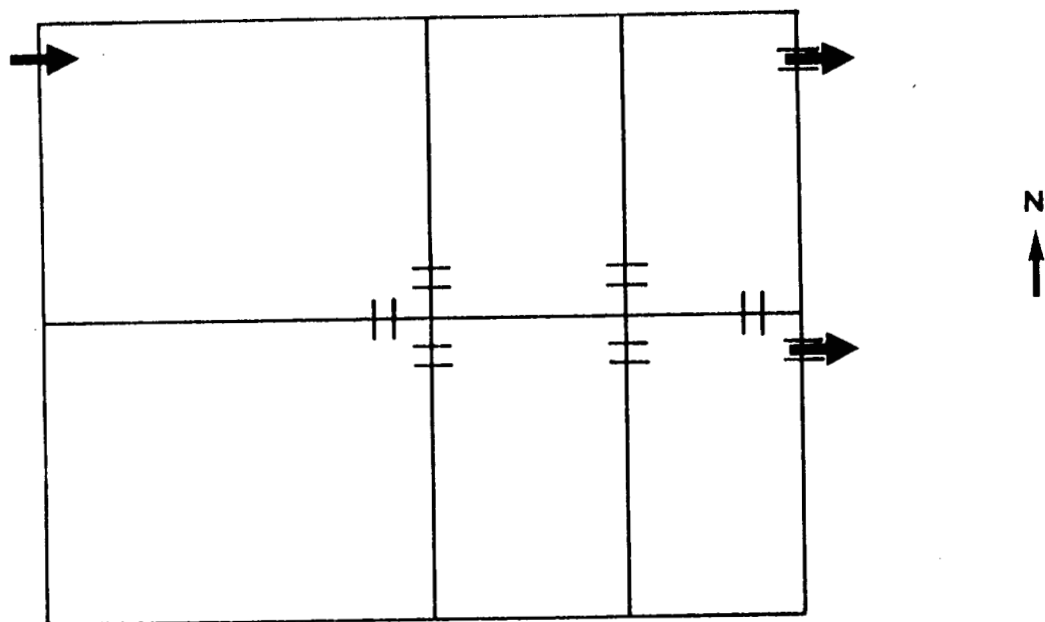


Figure 25. Flow field #16 (top) and field #17 (bottom) are 74 acres (30 hectares) and 94 acres (38 hectares), respectively. Molinate was applied 6/10/83 at 4 lbs AI/A. Arrows indicate field water inlets and outlets.

RESULTS

A. Mass Balance

Results from the molinate mass balance field are confounded by a duplicate application of molinate. On June 1, this field received 4 lbs AI/A. The application monitored in this study was conducted on June 6 with a 2.8 lbs AI/A application rate. Background molinate concentrations (June 1 to June 6) were monitored and used as a reference point. The results and discussion sections should be reviewed with this duplicate application in mind.

Results of the mass balance chemical analyses are shown in Figure 26. The concentration of molinate in water was highest on the day of application (3430 ppb). The background water concentration (taken June 5) was 1876 ppb, 4 days following the first molinate application. By day 4 (of the second application), water concentrations dropped to 1703 ppb. Water concentration steadily declined to 13 ppb on day 32. Soil concentrations rose to a peak of 2210 ppb on day 8 then declined to 656 ppb on day 32.

Background soil concentrations were similar to those found on day 0 (the mean = 1445 ppb). Apparently it took a few days before molinate was incorporated into the soil matrix. Molinate concentrations in vegetation rose within 24 hours after application (918 ppb) then slowly declined to 21 ppb on day 32. The background level (498 ppb) was similar to the concentration on day 2 (423 ppb). Air samples had the highest concentration on the day of application at 6.25 ppb and dropped to 0.73 ppb on day 3 (appendix E). In all 4 mass balance components (air, water, soil and vegetation), molinate dissipated fairly rapidly.

Phase partition coefficients (representing the relationship between two materials) are depicted in Figures 27 and 28. The soil/vegetation coefficients (Fig. 27) generally increased with time, indicating either a preferential partitioning of molinate into soil or molinate dissipates more readily from vegetation. Soil/water and vegetation/water coefficients (Fig. 27) were more difficult to interpret because of the 4 day holding period. Up through day 4, the soil/water coefficients were below one, yet they were rising. This implied that either molinate was partitioned into soil (versus water) or dissipated more readily from water during that time. The coefficients rose dramatically after 4 days due to the replacement of holding-water by uncontaminated water. The vegetation/water coefficients remained the same and below one up till day 32, when the phase partition coefficient equaled 1.6. The distribution of molinate between vegetation and water remained fairly constant with less incorporated into plants than dissolved in water. When water concentrations dropped, so did vegetation levels (but not as rapidly). Air/water and air/vegetation coefficients declined from day 0 to day 2 and were below one. Air/soil coefficients

MOLINATE CONCENTRATION OVER TIME

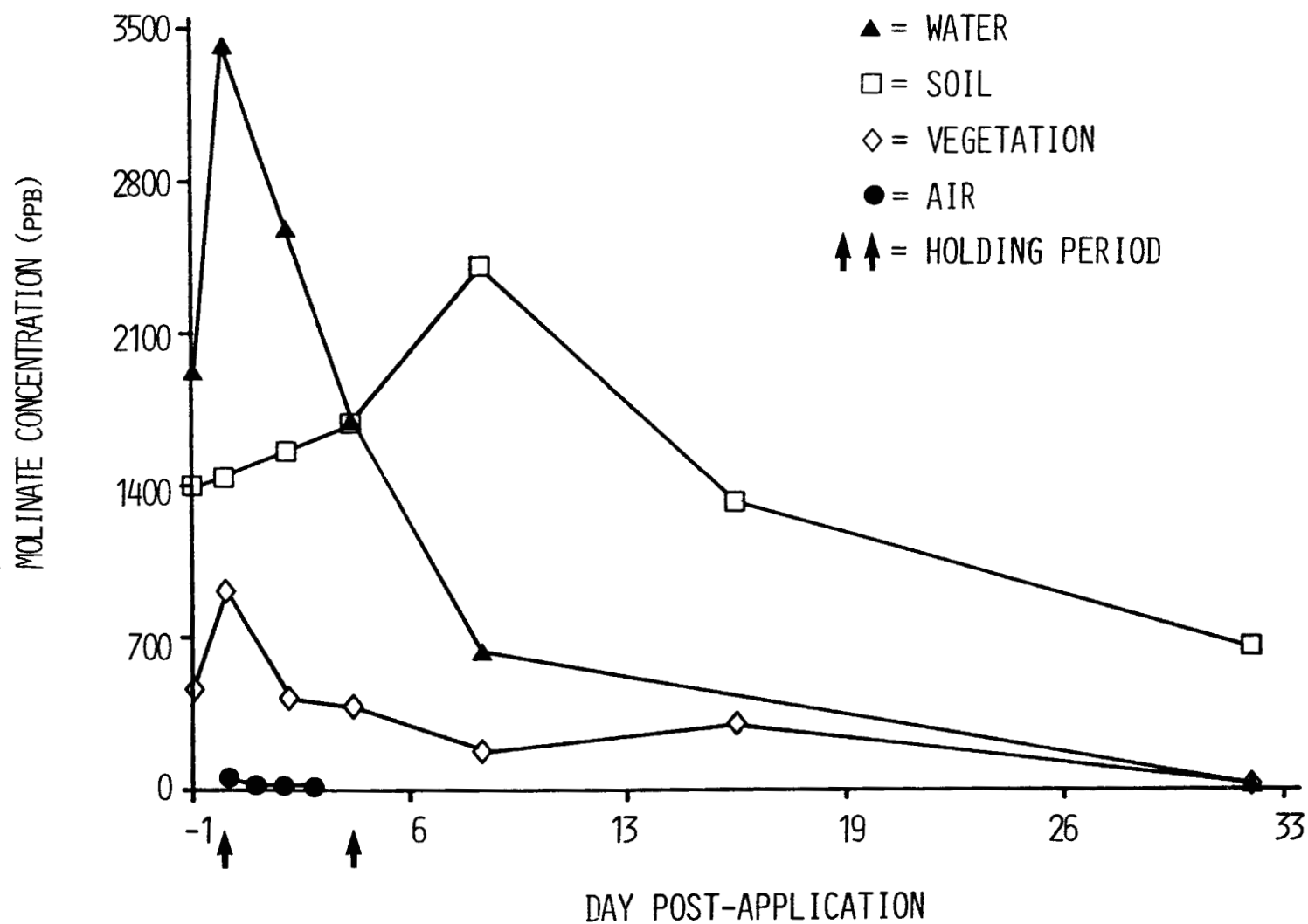


FIGURE 26. CONCENTRATION OF MOLINATE IN WATER, SOIL, VEGETATION AND AIR. EACH POINT IS A MEAN OF 16 SAMPLES COLLECTED FROM MASS BALANCE FIELD #4.

MOLINATE PHASE PARTITION COEFFICIENTS

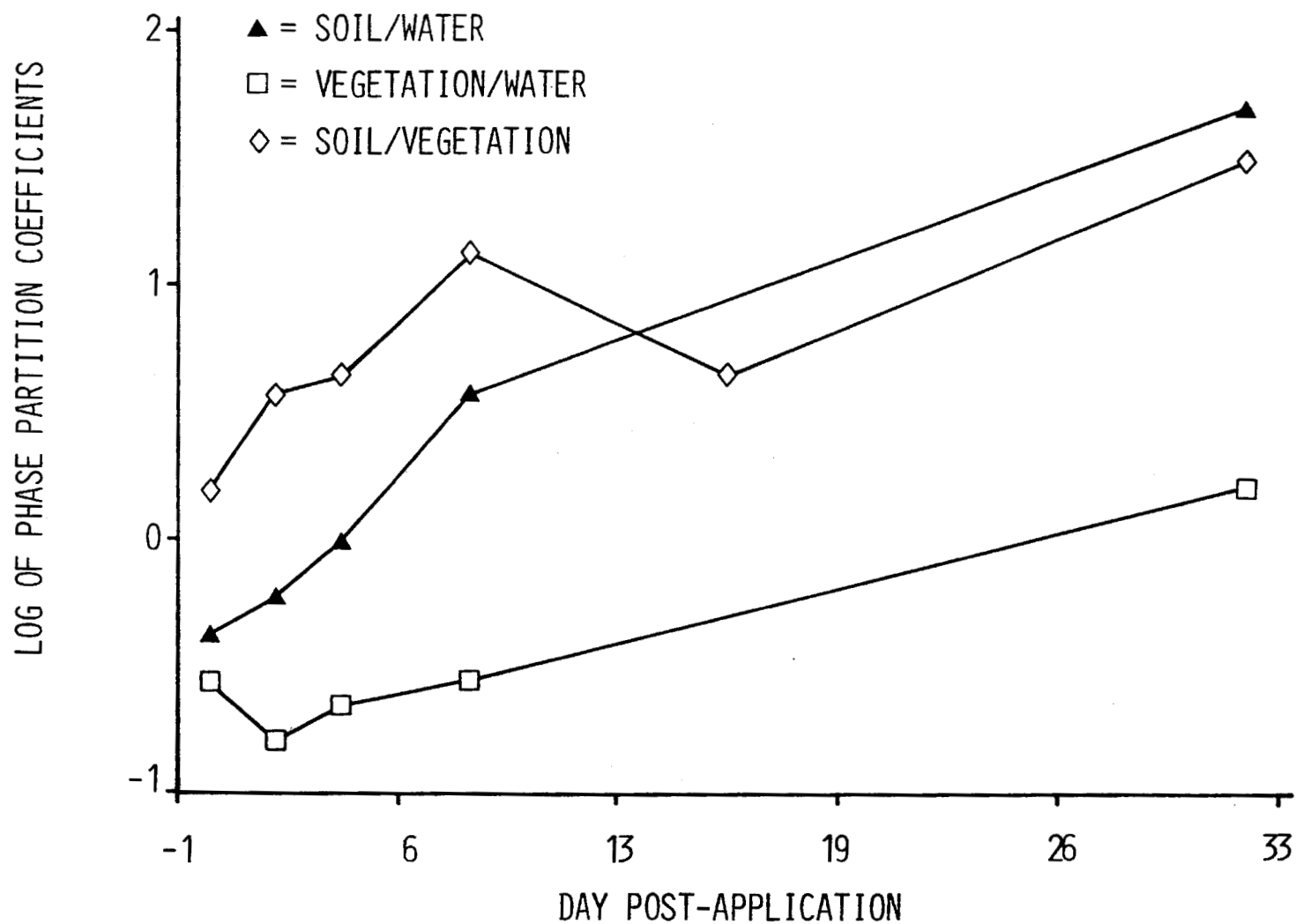


FIGURE 27. EACH MOLINATE PHASE PARTITION COEFFICIENT IS A RATIO OF THE VALUES DEPICTED IN FIG. 26.

MOLINATE PHASE PARTITION COEFFICIENTS

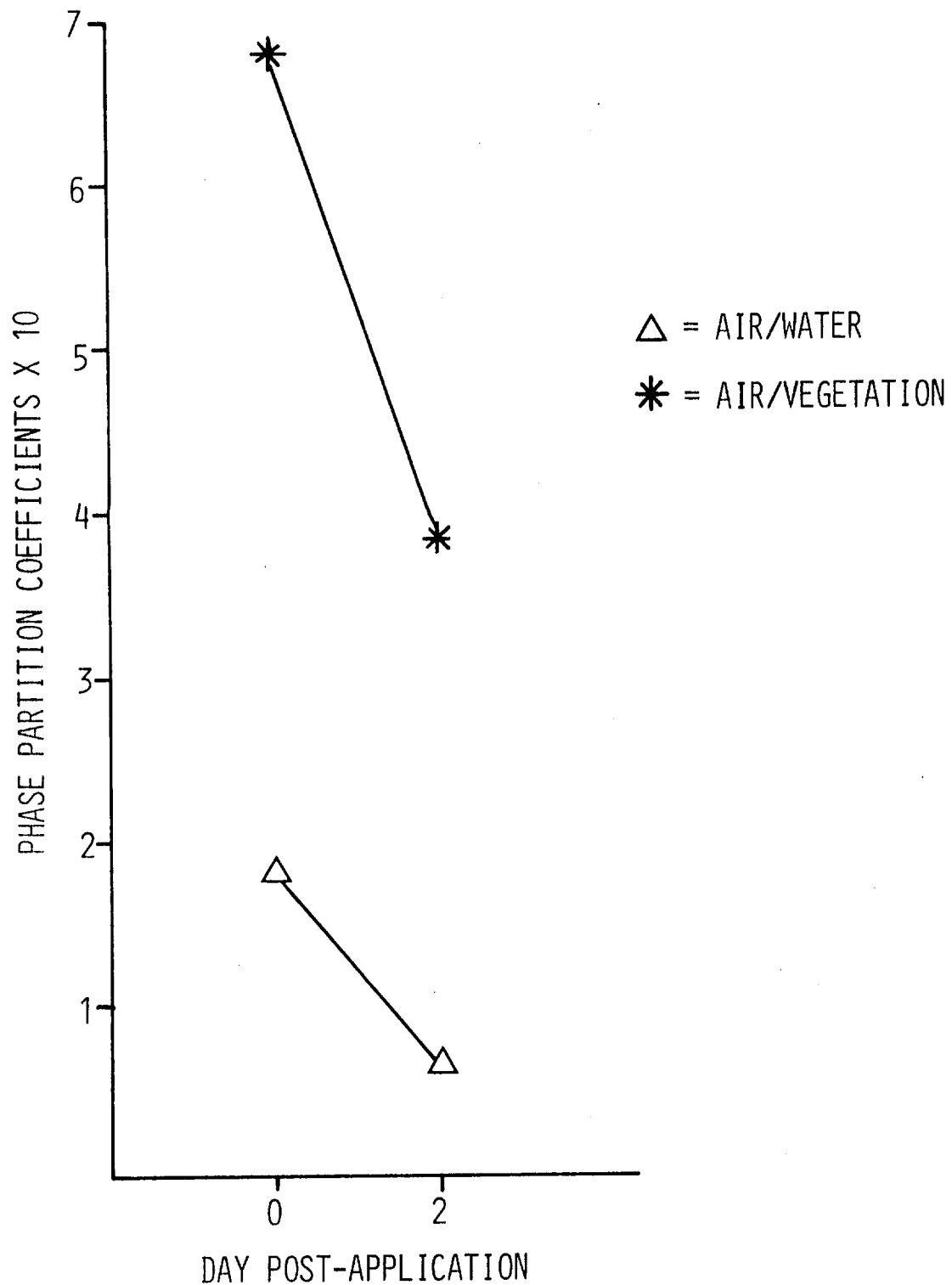


FIGURE 28. EACH MOLINATE PHASE PARTITION COEFFICIENT IS A RATIO OF THE VALUES DEPICTED IN FIGURE 26.

were not calculated since none of the thiobencarb in air was expected to evaporate from soil since it was covered with water during air sampling.

To determine the amount of molinate recovered in different components of the mass balance budget, the weight (kg) of molinate found in each medium was divided by the total weight recovered on day 0 (Fig. 29, see Part I, p.10 for details). (Day 0 was used as the denominator instead of the total amount applied because of the duplicate application.) A majority of molinate found in the field was located in the water component (75%, 51%, 36% on days 0, 2, and 4, respectively). A large proportion of molinate was lost to the air (17%) on the day of application, and declined on day 2 (to 3%). Soil contributed between 4% and 14% of the total mass balance budget. Vegetation comprised less than 0.01% of the total on any given day. After 32 days, only 4% of the total mass found on day one remained. This 4% was almost entirely in the soil component.

The ANOVA concerning molinate water concentrations (Table 8) indicated a significant difference among days post-application. There was a significant interaction between days and sites, but this seemed to be overridden by the effect of day on molinate concentration. Since there were no significant site effects, the 4 sites in each paddy were averaged to get a paddy concentration and the ANOVA was run again. By averaging the 4 sites, the problem of large variability in site observations obscuring paddy and day effects is removed. The new ANOVA design was the same as for thiobencarb (p. 22). Again, there was a significant difference in molinate concentrations among days. The DMRT showed day 0 had the highest molinate concentration. Days 2, 4, and -1 were next highest, followed by days 8 and 32. Water samples were not taken on day 16 because the field was completely drained at that time. Both t-tests were highly significant ($\alpha = 0.01$), indicating significant molinate degradation during the holding period as well as afterwards. The ANOVA for sulfoxide indicated a significant difference in days, sites and the site x day interaction. The DMRT for sulfoxide water concentration among days showed a similar pattern to molinate, just lagging behind a few days. Sites 1 and 3 had significantly lower sulfoxide concentrations than other sites (data not shown), but the reason for this was not apparent. The DMRT for site by day interaction reflected the trends seen in individual treatment effects (data not shown). The background molinate concentration in water, (day -1), coincided with 2 and 4 days post-application. This was not surprising since day -1 actually corresponds with 4 days following the first molinate application. This indicated the ability of molinate to dissipate readily even after back-to-back applications.

The ANOVA for soil (Table 9) indicated a significant difference among paddies, days, and sites in molinate concentration. The DMRT for paddies showed they were significantly different and paddy 4 contained nearly twice the

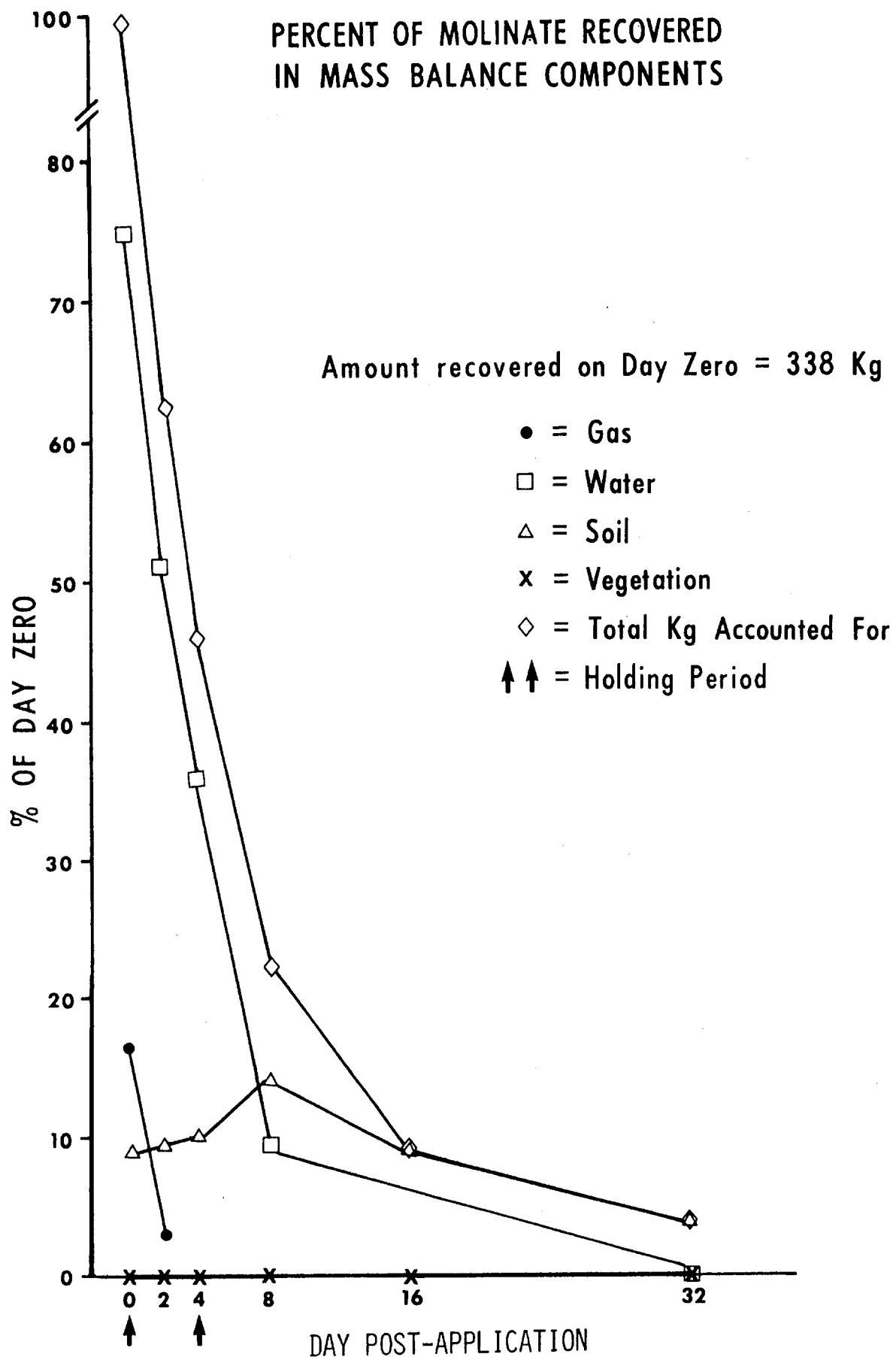


Figure 29. Mass balance budget of molinate. After day 4, water was released from the rice field. On day 16, the field was completely drained so no water sample was taken.

Table 8. Statistical Analyses of Molinate and Sulfoxide Concentrations in Water.

ANOVA Results

<u>Source of Variation</u>	<u>df</u>	<u>Molinate</u>	<u>Sulfoxide</u>	<u>df</u>	<u>Molinate</u>
		<u>F-test</u>	<u>F-test</u>		<u>F-test</u>
Paddy	3	2.60	0.70	3	2.24
Day	4	15.98**	9.19**	5	16.76**
Error	12			15	
Site	3	1.24	16.91**	3	N.A. ^{a/}
Site x Day	12	2.49*	4.65**	15	N.A.
Site x Paddy	9	1.53	1.68	9	N.A.
Error	36			45	N.A.

DUNCAN'S Multiple Range Test

<u>Day Post Application</u>	<u>Mean Molinate Concentration</u> (n=4)		<u>Mean Sulfoxide Concentration</u> (n=4)	
-1	1877	Y	7	B
0	3430	X	9	A B
2	2455	Y	13	A
4	1756	Y	14	A
8	655	Z	7	B
32	13	Z	0	C

Means followed by the same letter are not significantly different at the 5% level.

t-test

	<u>Molinate</u>		<u>Sulfoxide</u>	
	0 vs 4 days	8 vs 32 days	0 vs 4 days	8 vs 32 days
t' □	5.009**	7.321***	4.472**	7.000***

* □ Significant at the 5% level.
 ** = Significant at the 1% level.
 *** = Significant at the .1% level.
 a/ = Not applicable.

Table 9. Statistical Analyses of Molinate Concentrations in Soil.

ANOVA Results

<u>Source of Variation</u>	<u>df</u>	<u>F-test</u>
Paddy	3	9.56**
Day	6	3.84*
Error	18	
Site	3	8.43**
Site x Day	18	0.70
Site x Paddy	9	1.21
Error	54	

DUNCAN's Multiple Range Test

<u>Paddy #</u>	<u>Mean Molinate Concentration (n=28)</u>
1	1014 Z
2	1292 Z
3	1300 Z
4	2275 Y Z

<u>Day Post Application</u>	<u>(n=16)</u>
-1	1408 B
0	1445 B
2	1563 A B
4	1683 A B
8	2209 A
16	1329 B C
32	656 C

<u>Site #</u>	<u>(n=28)</u>
1	1227 F G
2	1664 E F
3	944 G
4	2047 E

Means followed by the same letter are not significantly different at the 5% level.

t-test

0 vs 4 days	8 vs 32 days
t' = 0.569	4.266***

* = Significant at the 5% level.
 ** = Significant at the 1% level.
 *** = Significant at the .1% level.

amount of molinate of any other paddy. This paddy was at the edge of the field and may have received extra herbicide to combat heavy weed growth. (Edges of a field typically contain a greater percentage of weeds.) The DMRT for days post-spray showed a good deal of overlap. Day 9 had the highest soil concentration, followed by days 4 and 2. Rather than flow off with the holding water, molinate may have repartitioned into the soil. Soil concentrations increased up through day 8 but on day 16, concentrations dropped. This drop may have been related to the complete drainage of that field on day 16. Once drained, molinate may have evaporated from the soil into the air and/or degraded via aerobic microbial organisms. On day 32, soil concentrations dropped still further and were significantly lower than on day 8 (t-test, $\alpha = 0.001$). Sites were also significantly different and the DMRT indicated site 3 had the lowest and 4 had the highest soil concentrations. However, there were no site by paddy interactions.

Table 10 shows results from statistical analyses conducted on vegetation. Molinate concentration in vegetation was significant among days. The DMRT indicated peak vegetation concentrations on the day of molinate application. Day -1 overlapped day 0, yet also overlapped days 2, 4, 8, and 16. The concentration of molinate in vegetation did not change significantly during the holding period but vegetation sampled on day 32 had significantly less molinate than on day 8 (t-test, $\alpha = 0.001$), indicating it dissipated readily even after a double application.

B. Flow Fields

Results from flow field monitoring are depicted in Figures 30 through 38. Most fields had a markedly different drain flow pattern. Fields 6, 8 and 12 were the only similar ones with flows near 20 l/sec at the end of the holding period, and subsequent flow rates mostly between 10 and 50 l/sec for the remainder of the sampling period. No other fields had an obvious flow pattern and drain flow rates often dropped to 0 at sporadic intervals.

Concentration of molinate at drains showed a general decline over time for all flow fields. Occasionally there was an increase in concentration after levels dropped below the MDL (5 ppb). Usually those increases were not above 10 ppb, an insignificant increase in concentration.

Flux calculations varied with concentration and/or flow, depending on the magnitude of those values. When drain flows were erratic (as in a majority of fields), so were flux calculations. In fields 6, 8 and 14, where drain flow rates were fairly uniform, flux curves were similar to concentration

Table 10. Statistical Analyses of Molinate Concentrations in Vegetation.

ANOVA Results

<u>Source of Variation</u>	<u>df</u>	<u>F-test</u>
Paddy	3	1.29
Day	6	3.97*
Error	18	

DUNCAN'S Multiple Range Test

<u>Day Post Application</u>	<u>Mean Molinate Concentration (ppb)</u> (n=4)
-1	498 X Y
0	918 X
2	423 Y Z
4	380 Y Z
8	177 Y Z
16	295 Y Z
32	21 Z

Means followed by the same letter are not significantly different at the 5% level.

<u>t-test</u>	0 vs 4 days post-application	8 vs 32 days post-application
t' =	1.618	7.026***

- * Significant at the 5% level.
 ** Significant at the 1% level.
 *** Significant at the .1% level.

Ordram Field #1

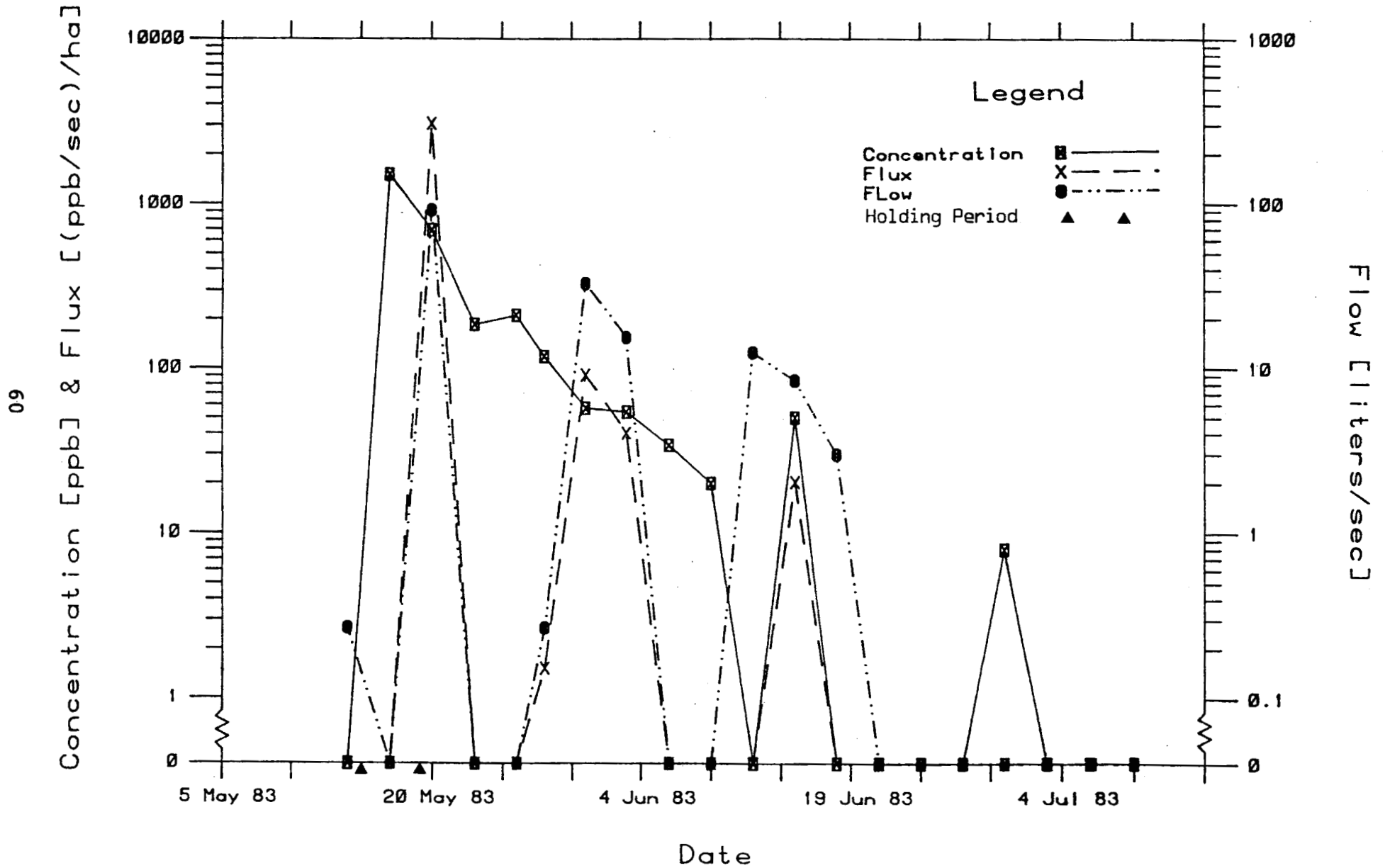


Figure 30. Molinate flow field #1. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Ordram Field #5

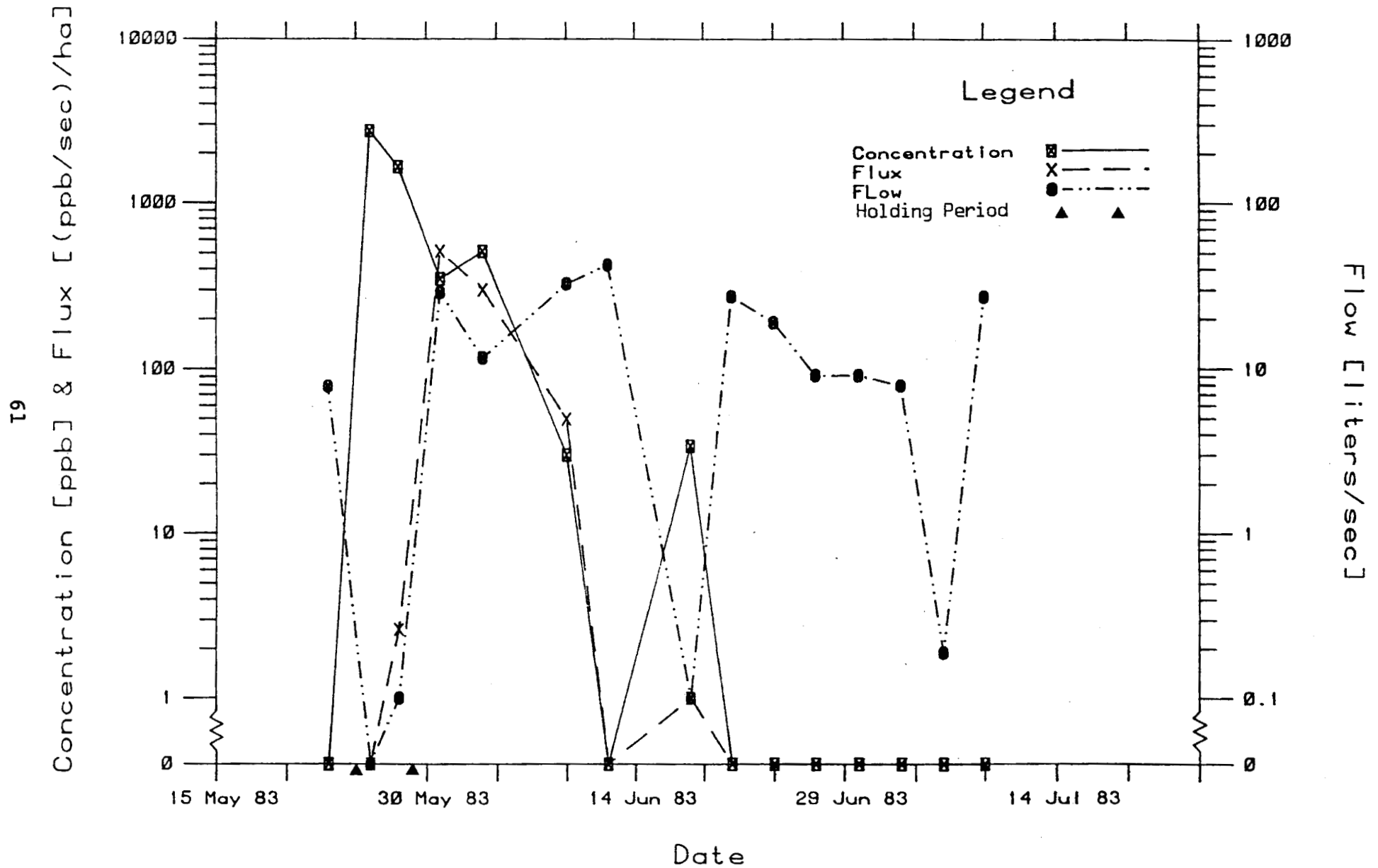


Figure 31. Molinate flow field #5. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Ordram Field #6

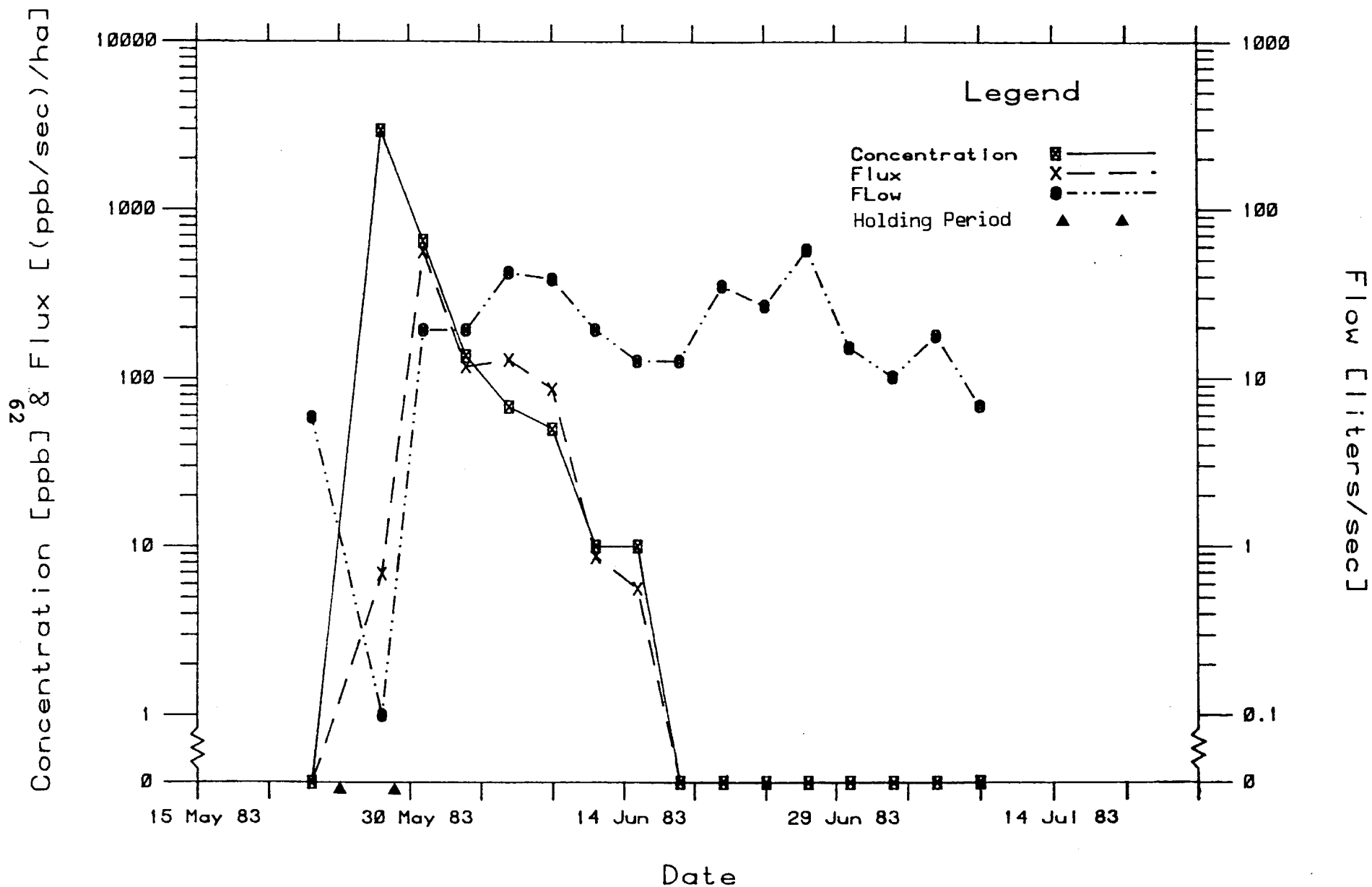


Figure 32. Molinate flow field #6. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Ordram Field #8

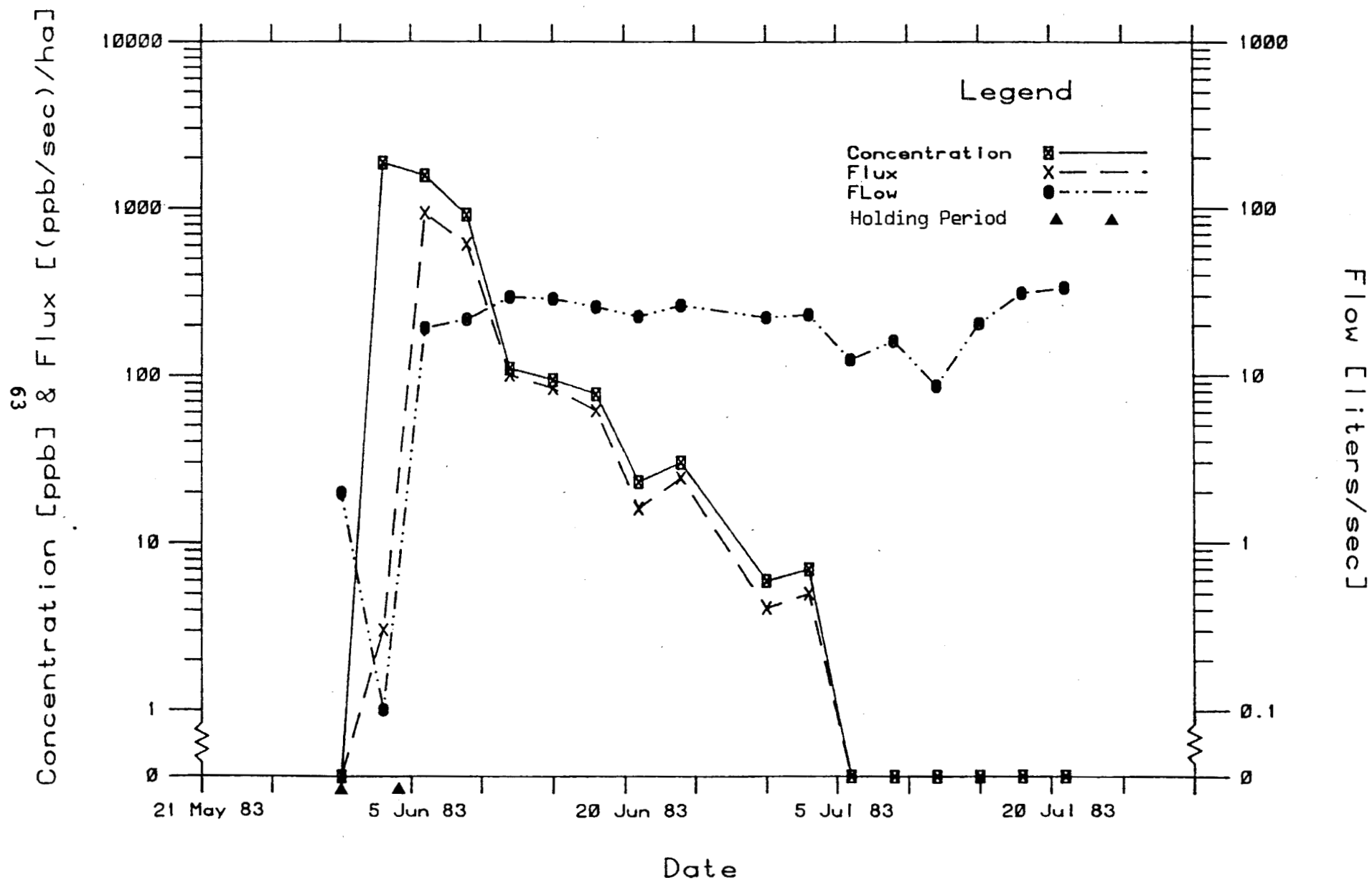


Figure 33. Molinate flow field #8. Concentration (ppb) and flux [(ppb/sec)/ hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Ordram Field #11

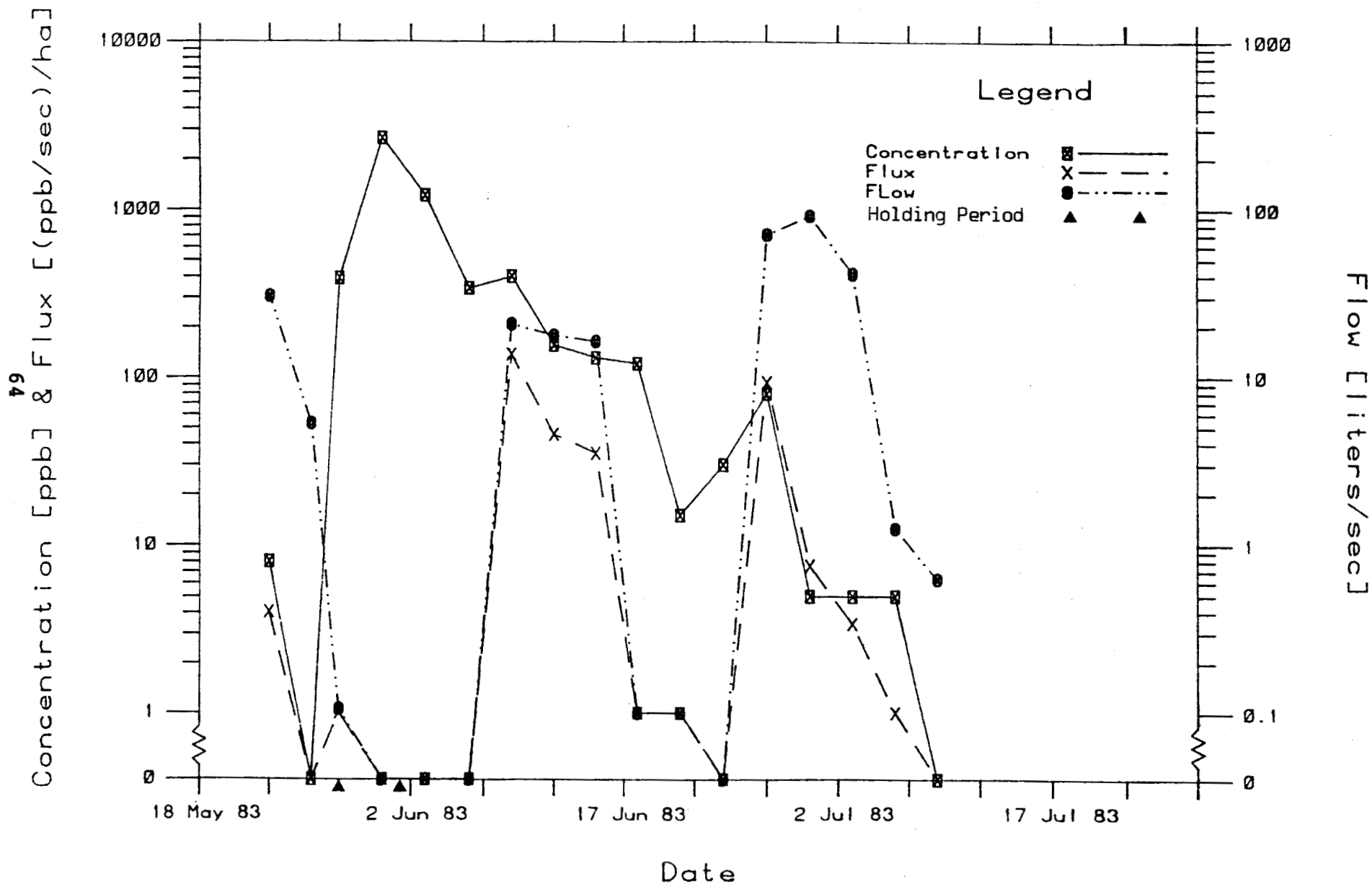


Figure 34. Molinate flow field #11. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Ordram Field #12

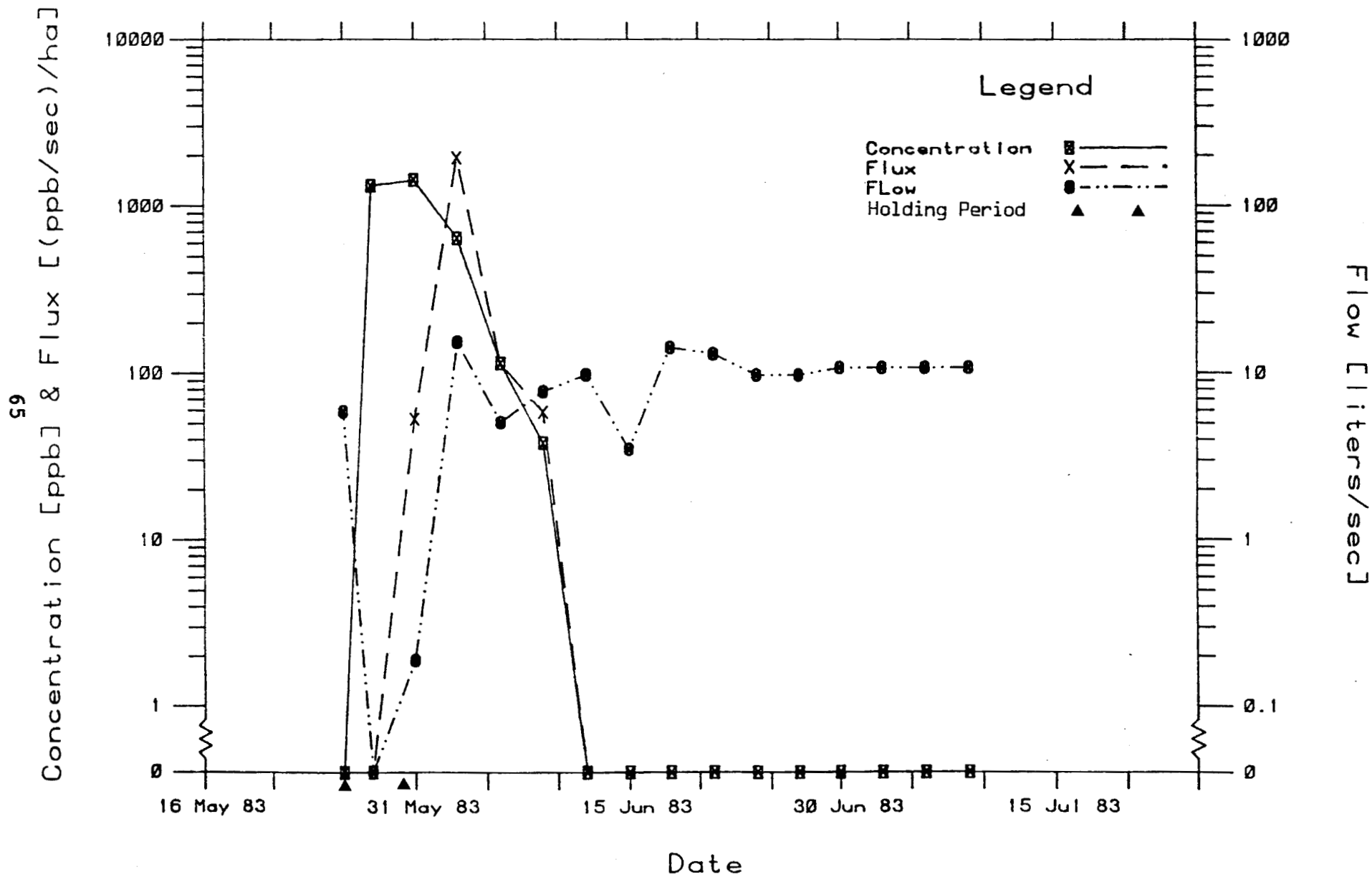


Figure 35. Molinate flow field #12. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Ordram Field #15

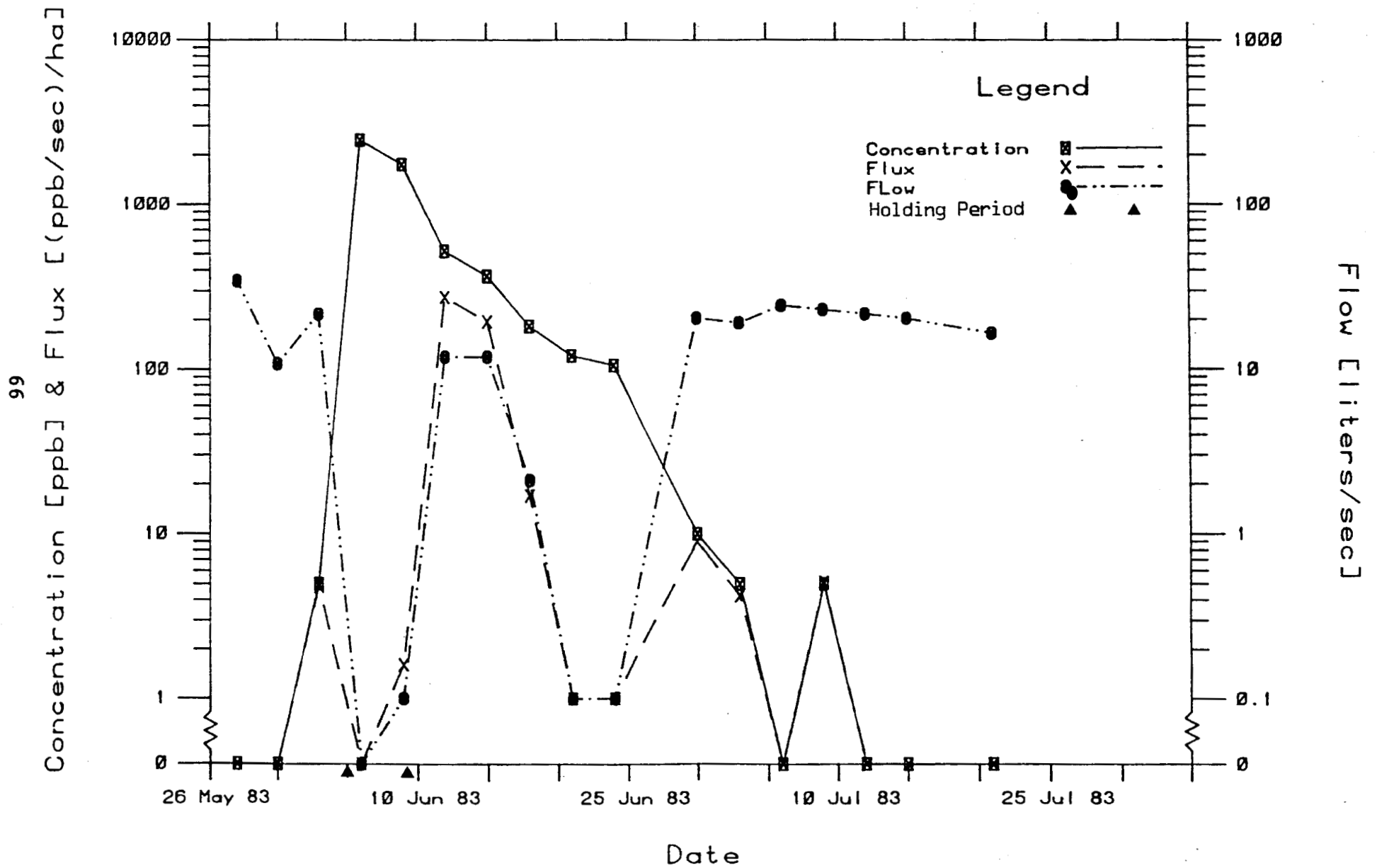


Figure 36. Molinate flow field #15. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Ordram Field #16

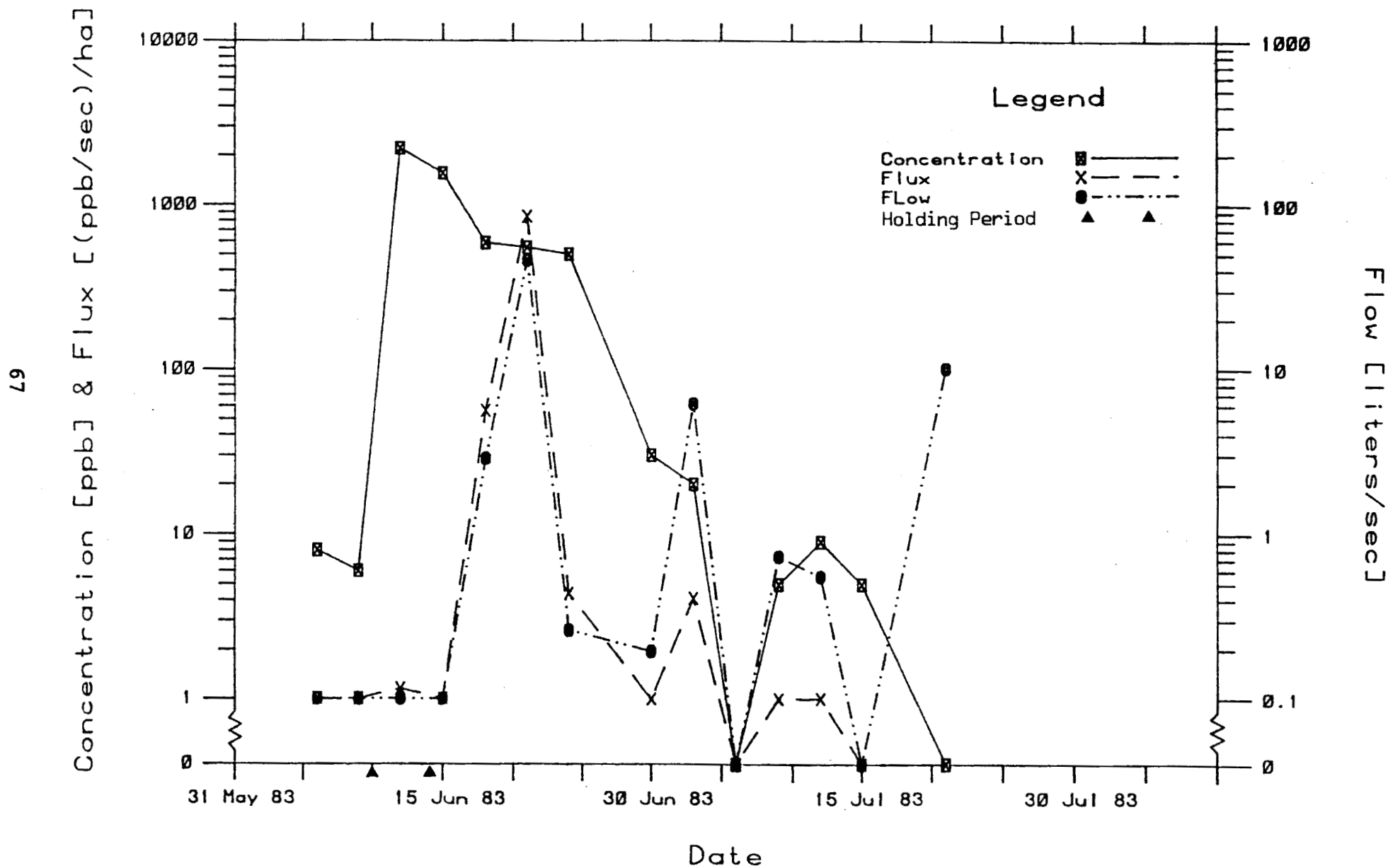


Figure 37. Molinate flow field #16. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

Ordram Field #17

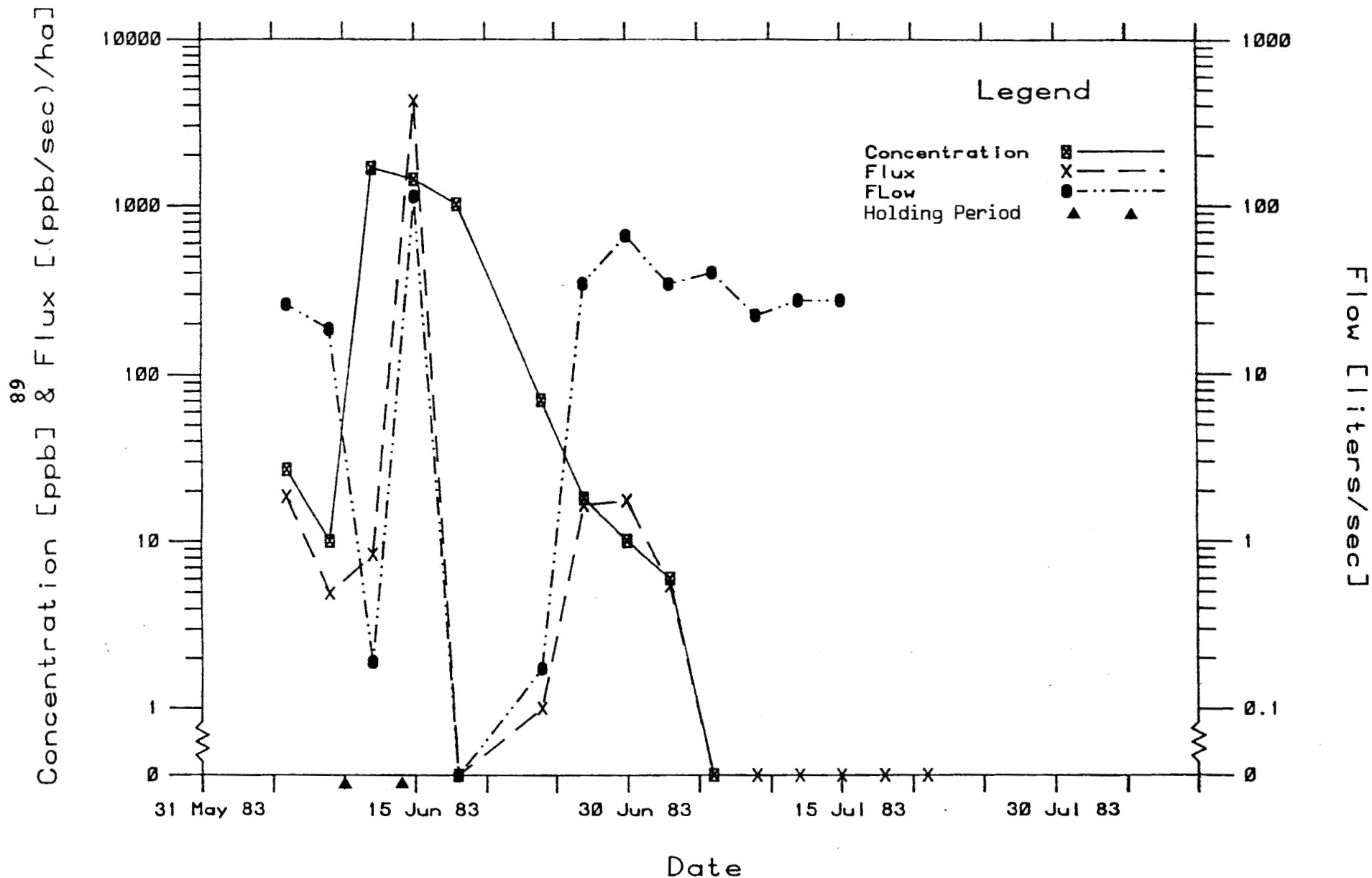


Figure 38. Molinate flow field #17. Concentration (ppb) and flux [(ppb/sec)/hectare] are on the left y-axis and flow (liters/sec) is on the right y-axis. Arrows on the x-axis indicate the holding period.

curves.

Due to the erratic pattern of flux values in 6 of 9 flow fields, an equation predicting molinate flux from a "typical" field could not be developed. Instead, we attempted to predict molinate concentration (at the drain) of a "typical" rice field. Independent variables used to predict molinate concentration were the same as for thiobencarb (see Part I).

The volume of water standing on a field ranged from 1×10^6 to 5×10^7 l, depending on field size and water depth. Net flow was often a negative rate (i.e. more water flowing onto than off a field). Evaporation, transpiration and grower manipulation of inflow and outflow rates were largely responsible for that condition.

Stepwise linear regressions were run on individual fields to determine if any similarities existed among them. Results of these runs are shown in Table 11. Day 0 (day of application) was omitted from the regression analyses for reasons described in Part I (p. 27). The stepwise regression program entered the log of and square root of day post-application in all (best) regression equations, implying these were the most important variables in predicting molinate concentration. All equations had significant F values at the 1% level. To determine similarity among equations, twice the standard error of the coefficient was added and subtracted from its respective coefficient. This procedure yielded a rough 95% confidence limit around each coefficient. The overlap of these confidence limits indicated that the regression equations were similar enough to combine all fields into a single equation.

To create a single equation predicting molinate concentration at field drains, all variables were averaged by day among fields. These averages were then entered into the regression program and the final equation is shown in Table 11. The R^2 value indicated the combined equation captured a great deal of the variation in the dependent variable. The low SEE (183 ppb) also indicated the equation was a fair predictor of molinate concentration. Figure 39 depicts observed and predicted concentrations over time.

Mass discharge of molinate from flow fields was also calculated. To determine the amount of molinate (kg) leaving a field, flow rates were multiplied by drain concentrations, then extrapolated over a 24 h period. This daily value is a very rough estimate of mass discharge per day. Table 12 contains a summary of that information. Mass discharge for the month following molinate application ranged from 0.2 to 49.4 kg. The amount discharged in one month ranged from 0.2 to 29% of the total applied. Beyond 1 month, weekly mass discharge was below 1% of the total applied.

Table 11. Molinate Flow Field Regression Equations

Field #	Equation ^{a/}	S.E.E. ^{b/}	S.E.C. ^{c/}		R ^{2d/}
			Log	Sq. Rt.	
1	y= 2318 - (3638 Log Day)+(557 Sq.rt.day)	86	312	62	.95
5	y= 3485 - (6156 Log Day)+(1026 Sq.rt.day)	161	598	136	.97
6	y= 5666 - (10498 Log Day)+(1796 Sq.rt.day)	288	1569	320	.88
8	y= 4217 - (6257 Log Day)+(923 Sq.rt.day)	170	820	160	.93
11	y= 5360 - (9131 Log Day)+(1498 Sq.rt.day)	163	956	200	.96
12	y= 2630 - (3910 Log Day)+(578 Sq.rt.day)	197	895	192	.86
15	y= 3334 - (5131 Log Day)+(781 Sq.rt.day)	156	547	122	.96
16	y= 3719 - (5253 Log Day)+(750 Sq.rt.day)	133	704	157	.97
17	y= 3091 - (4172 Log Day)+(568 Sq.rt.day)	189	964	214	.92
All	y= 3588 - (5940 Log Day)+(960 Sq.rt.day)	183	711	179	.94

a/ The estimate y= the concentration of thiobencarb in ppb.

b/ SEE = Standard error of the estimate.

c/ SEC = Standard error of the coefficient.

d/ R² is the proportion of the variance of the dependent variable explained by the regression equation.

MOLINATE CONCENTRATION AT DRAIN,
PREDICTED AND OBSERVED VALUES.

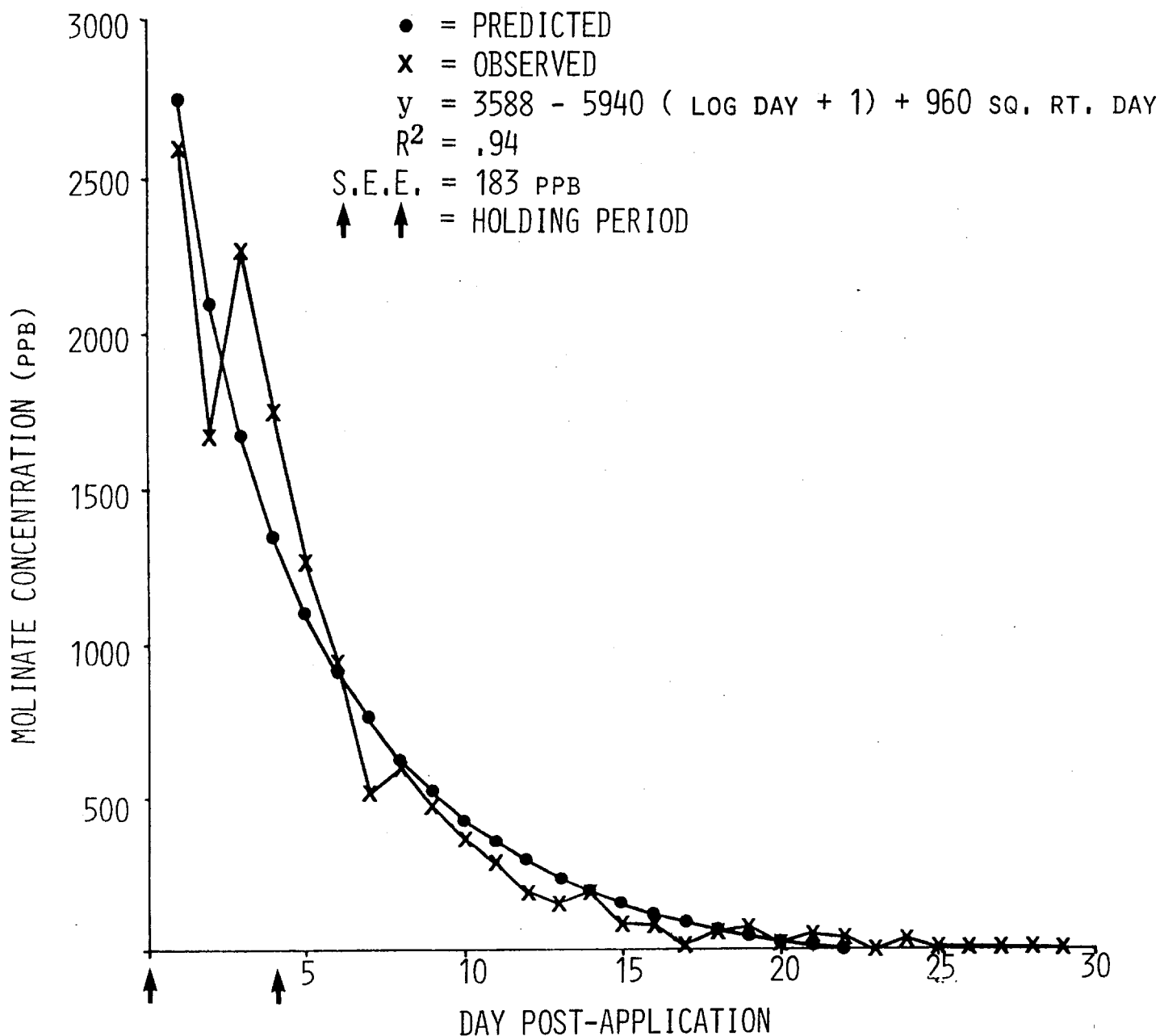


FIGURE 39. OBSERVED (x) AND PREDICTED (•) MOLINATE CONCENTRATIONS AT THE DRAIN OF FLOW FIELDS. OBSERVED CONCENTRATIONS WERE AVERAGED AMONG FIELDS (N = 1 TO 4) BY DAY. S.E.E. = STANDARD ERROR OF THE ESTIMATE (y).

Table 12. Molinate Mass Discharge From Flow Fields

Field #	Kg. Applied	Amount of Molinate Discharged (Kg)	Theoretical Discharge for 4 Weeks (Kg)	% of Applied
1	92	5.69 (7) ^{a/}	22.76 ^{b/}	25 ^{c/}
5	88	1.48 (7)	5.93	7
6	94	1.78 (9)	0.20	0.2
8	144	5.13 (9)	15.97	11
11	269	1.63 (8)	5.71	2
12	23	0.95 (9)	2.96	13
15	100	0.97 (7)	3.88	4
16	133	2.36 (7)	9.43	7
17	169	14.12 (8)	49.42	29

^{a/} Numbers in parentheses = the number of days summed into the amount of Molinate discharged.

^{b/} Values in this column were calculated by multiplying the mean amount of Molinate discharged by 28 (the number of days in 4 weeks).

^{c/} Percentages in this column = theoretical discharge for 4 weeks divided by total Kg applied.

DISCUSSION

From the ANOVA tests it appears that molinate dissipates below background levels quite rapidly in water and vegetation. After 4 days into the holding period, water concentrations dropped 49% and vegetation dropped 59% (only water was significant). Soil concentrations increased during the holding period but did decline 55% by day 32 (significant at the 0.1% level).

Water and vegetation concentrations declined continually throughout the month and by day 32, had dropped 99.6% and 97.7% from levels found on day 0, respectively. However, water concentrations recorded beyond 4 days inevitably reflect termination of the holding period. Uncontaminated water (molinate below the MDL) replaced molinate-laden water, thereby lowering the concentration via dilution and mass flow. Vegetation concentrations may have also responded to this as indicated by the phase partition coefficients. It is possible that plant growth over the course of the month may provide a dilution factor for the concentration of molinate in vegetation.

Soil concentrations did not decline as rapidly as water or vegetation components. During the holding period, soil concentrations increased 16% and by day 8, had increased 53% over levels found on day 0. On day 16, the field was drained completely and soil concentrations decreased 55% of those found on day 0. Studies have shown that under anaerobic conditions (i.e. soil under water), degradation of molinate is slower than under aerobic conditions (19 and 20). Therefore, the exposure of soil to air prior to day 16 may have caused the drop in concentration (via the more rapid aerobic degradation pathway).

The DMRTs and ANOVAs bring out another interesting point. For the water and vegetation components, concentrations found on day 4 were not significantly different from background levels. (Background levels equal day 4 after the second application). This implies that even with duplicate applications of molinate, occurring within 5 days of each other, dissipation is still fairly rapid in water and vegetation. However, soil concentrations steadily increased until the field was drained. We don't know what the soil levels would have been, had the field not been drained.

Mass discharge calculations indicate 11% of the total amount of molinate applied to a field leaves in drain-flow water within the first month after application. However, this percentage is extrapolated from 7 to 9 days of data collection (plus, these were "grab" samples, i.e., taken at one point in time on one day), so it is merely a rough estimate of discharge. Of the samples collected that first month, 69% of the molinate reported leaving the field was captured between 5 and 7 days

post-application. This implies that the holding period water contributes a major portion of the mass discharge. The rest is probably repartitioned from soil back into water over the course of the month. Molinate mass discharge (in water) declines to below the MDL by day 39 in all fields. Therefore, it is likely that our 11% estimate (cited above) is low since we did not intensively sample immediately following the holding period.

Molinate is 100 times more volatile above water than is thiobencarb. Henry's Law constant = 1.7×10^{-7} atm.m³/mole (a vapor pressure/water solubility ratio, see Part I, p. 37). The % of molinate lost to air was lower when the comparison was made between air flux and the total amount of herbicide applied rather than with respect to the amount of molinate in water (which is available for volatilization). The maximum concentration of molinate reported by Dr. Seiber was 6.3 ppb on the day of application. In terms of the total amount of molinate found on day 0, the amount evaporating was 16.6% but based on the amount in water, it was 22%. These figures, based on the amount found on day 0, are confounded by the double application of molinate. If the background water concentration is subtracted from concentrations reported for day 0, the amount of molinate evaporating is 40 and 56%, respectively. At 0 days post-application, these values drop to 3.3 and 6.3% (using the amount of molinate found on day 0 as the denominator), respectively. The large drop in % from 0 to 2 days post-application was probably due to the decline in molinate flux (see Appendix A, p.94). This decline in flux probably occurred for the same reasons outlined in Part I (p. 37).

The mass balance budget is also indicative of rapid dissipation of molinate in water and air. The air component is much larger here than for thiobencarb, reflecting its higher vapor pressure density. However, it is important to examine volatilization of molinate with respect to water, the medium from which it volatilizes (see above). Water concentrations rapidly dissipate within the 4 day holding period. Afterwards, degradation, dilution and mass flow contribute to the decline in water concentrations.

Again, as in thiobencarb mass balance, we find that vegetation comprises a very small amount of the budget. On all days, vegetation never accounted for more than 0.01% of the total budget. A possible explanation (which may also apply to thiobencarb) involves 2 processes: 1. the plant stage when molinate is applied and 2. volume changes in plant biomass. When plants are in an immature growth stage and have little biomass (therefore low density and small volume) they are often sprayed with molinate. Therefore, the time of maximum molinate uptake coincides with the lowest plant volume. When plants are mature, less molinate is taken up (less is available) and plant volume increases. In both immature and mature stages, the mass balance figures would be low due to the interplay of volume and maximum herbicide uptake. The concentration of molinate in vegetation is

not that much less than concentrations found in soil during the holding period, or water after the holding period. However, in the mass balance scheme, vegetation (with its low volume) contributes less than 1% to the total budget.

Predicting molinate concentration at field drains using a least squares linear regression equation was much more accurate than for thiobencarb. The high R^2 value indicates the equation fit the observed data points very well. The SEE about the mean concentration is fairly good considering the magnitude of the mean (476 ppb). Therefore, with a good R^2 value, significant regression equation and a low SEE, this equation has potential for use in predicting molinate concentrations at field drains.

Molinate, (unlike thiobencarb), dissipates fairly quickly in water and vegetation. Less than 1% of the peak water concentration and 2% of peak vegetation concentration remain in these components after 1 month. Little molinate remains in water at the end of the month because of dilution and mass flow of herbicide-laden water off the rice field. However, when water is held on the field for 4 days, only 51% of peak water concentrations remain. Only 30% of the peak soil concentration remains after 1 month, but this value may be low because the field was completely drained during the month. Only about 4% of the molinate found on the day of application remains on the field after 1 month, 96.6% of which is in soil. From this study it appears that molinate readily dissipates from rice field components.

REFERENCES

1. California Department of Water Resources, Northern District. 1982. Low applied water on rice. Published Report.
2. Ratger, J. N. and D. M. Brandon. Feb. 1981. California rice culture. Scientific American: 43-51.
3. Hill, J. M. 1984. Cited in: Lee, M. 1984. Molinate and thiobencarb: A review of their use and off-site movement. Report. Environmental Monitoring and Pest Management. CDFA, 1220 N St., Sacramento, CA 95814.
4. University of California Statewide Integrated Pest Management Project, Division of Agricultural Sciences. 1983. Integrated Pest Management for Rice. Publication 3280.
5. State Water Resources Control Board, Toxics Special Project. 1984. Rice herbicides ordram (molinate) and Bolero (Thiobencarb). A water quality assessment. Draft Report.
6. Tanji, K. K., M. J. Singer, L. D. Wittig, J. W. Biggar, D. W. Henderson and S. A. Mirbagheri. 1982. Nonpoint sediment production in the Colusa Basin drainage area. Final Technical Completion Report to the U.S. EPA. Department of Land, Air and Water Resources, University of California, Davis, Water Science Engineering Paper ab. 4016. 266 pp.
7. Finlayson, B. J. and T. L. Lew. 1983b. Rice herbicide concentrations in Sacramento River and associated agricultural drains. California Department of Fish and Game, Environmental Services Branch, Administrative Report No. 83-7.
8. Varozza, J.F. City Engineer, Department of Engineering, 915 I Street, Sacramento, CA 95814. Aug. 2, 1984. Status report to the City Council, Sacramento, California, concerning the rice herbicides, Bolero and ordram.
9. Finlayson, B. J., J. L. Nelson, and T. L. Lew. 1982. Colusa Basin drain and reclamation slough monitoring studies, 1980 and 1981. California Department of Fish and Game, Environmental Services Branch, Administrative Report No. 82-3.
10. Finlayson, B. J. and T. L. Lew. 1983a. Rice herbicide concentrations in Sacramento River and associated agricultural drains. California Department of Fish and Game, Environmental Services Branch, Administrative Report No. 83-5.
11. California Department of Food and Agriculture. 1982. California agricultural summary. CDFA, 1220 N Street, Sacramento, CA 95814.
12. Sokal, R. R. and F. J. Rohlf. 1969. Introduction to Biostatistics. p. 170-5. W. H. Freeman and Company, San Francisco. 308 pp.

REFERENCES (con't)

13. Dixon, W. J., Chief Editor. 1981. BMDP Statistical software. University of California Press, Berkeley, CA 726 pp.
14. Hartley, G. S. and J. J. Graham-Bryce. 1980. Physical principals of pesticide behaviour. Volume 1. Academic Press, Inc. 111 Fifth Ave., New York, NY 10003. 518 pp.
15. Chevron Chemical Company. 1983. Data summaries for Bolero 10G. Chevron Chem. Co., Richmond, CA.
16. Nakamura, Y., K. Ishikawa and S. Kuwatsuka. 1974. Uptake and translocation of benthiocarb herbicides by plants. *Agricultural Biology and Chemistry* 38(6):1129-1135.
17. Chevron Chemical Company. 1979. Data summaries for Bolero 10G. Herbicides for use on rice. Residues and plant metabolism section: p. 005-007.
18. Nakamura, Y., K. Ishikawa and S. Kuwatsuka. 1977. Metabolic fate of binthiocarb herbicide in plants. *Agricultural Biology and Chemistry*. 41:1613-1620.
19. Thomas, V. M. and C. L. Holt. 1980. The degradation of (¹⁴C) molinate in soil under flooded and nonflooded conditions. *Journal of Environmental Science and Health B15(5):475-484*.
20. Imai, Y. and S. Kuwatsuka. 1982. Degradation of the herbicide molinate in soils. *Journal of Pesticide Science* 7:487-497.

A P P E N D I X A

Determination of Evaporative Flux for Thiobencarb and Molinate Were Calculated by J.N. Seiber, J.E. Woodrow, and M. McChesney in a Manner Similar to the Methods Described in the Following Report:

"Measurement of Evaporative Flux of MCPA and two Transformation Products From a Commercial Rice Field."

MEASUREMENT OF EVAPORATIVE FLUX OF MCPA AND TWO
TRANSFORMATION PRODUCTS FROM A COMMERCIAL RICE FIELD

James N. Seiber, James E. Woodrow and Michael M. McChesney

Department of Environmental Toxicology
University of California
Davis, California 95616

Report submitted to:

Environmental Hazards Assessment
Department of Food and Agriculture
1220 N Street
Sacramento, California 95814

January 20, 1984

OBJECTIVES

The MCPA flux study was done as part of a larger rice herbicide monitoring project conducted by the State of California Department of Food and Agriculture's Environmental Hazards Assessment group.

The objectives were:

1. Obtain air samples necessary for calculating MCPA herbicide and transformation products at a commercial rice field.
2. Analyze for MCPA and 4-chloro-o-cresol (4-ClOC) in the MCPA air samples.
3. Calculate flux for up to 4 days after treatment from resulting data.

DESCRIPTION OF FIELD

The experimental site, ca. 90 acres, was located on the Gordon Wiley Ranch in Glenn County. Field dimensions were ca. 0.3 mile \times 0.47 mile. A pier measuring 24 ft. \times 24 in. was constructed on a center check midway between north and south edges of the field. The pier extended into the water from the east side of the check. The prevailing wind was from the southeast, thus there was no apparent hindrance of fetch.

EQUIPMENT AND SUPPLIES USED DURING SAMPLING

XAD-4 resin:	Acid and base washed; Soxhlet extracted with methanol, then with diethyl ether.
High volume air samplers:	Bendix high volume samplers; one placed 19 inches above surface of the water and one at 77 inches above the water. Each sampler contained 100 ml of XAD-4 resin. Flow rate was 1 m ³ /min.
Low volume air samplers:	Each of two B.G.I. high volume air samplers was modified to operate three low volume sampling cartridges placed at 19, 36, and 77 inches above the surface of the water. Each cartridge contained 60 ml of XAD-4 resin. Flow rates were adjusted to 40 to 60 liters/min and the exact values were recorded.
Honda generators:	1500 watts with the voltage set at ca. 115 volts. Each generator ran two air samplers.
Solvents:	Solvents used to rinse sampling equipment between samples were Baker resi-grade or the equivalent.
Meteorological data:	<p>Temperatures were measured at 19 and 77 inches above the water using mercury laboratory thermometers. Aluminum foil was placed over, but not touching, the bulb end of the thermometer so that air could be free to come in contact without direct solar radiation.</p> <p>Wind speed was measured with 3-cup anemometers at both heights. Continuous readings were fed to a chart recorder and wind speeds were read directly off the chart and the average speed was estimated.</p> <p>Humidity, vertical wind deflection and wind direction were also measured at the high level.</p>

SAMPLING PROCEDURES

Background air samples:

Background air samples were taken on June 21, 1983 using Bendix high volume air samplers both at the pier and downwind of the field (60 and 210 ft. from the north edge of the field).

Air samples during spraying:

MCPA was applied on June 22, 1983 at 6:15 a.m. Application rate was 1 1/2 pints/acre of 48.6% dimethylamine salt of MCPA (Platte Chemical Co., Fremont, Nebraska). Downwind high volume air samples were taken during the 45 minute application period (60 and 210 ft. from the north edge of the field).

Air samples post spray:

High volume air samples were taken for a one hour period following the application at the downwind location.

Air sampling for flux:

High volume (1 m³/min) and low volume (ca. 50 l/min) air samples were taken from June 22 through June 25, 1983.

Each sampling period consisted of the following samples:

1. High volume air: 1 each at 48 and 195 centimeters
2. Low volume air: 2 each at 48, 91, and 195 centimeters

Downwind air, post spray:

Downwind high volume air samples were taken on June 23 and June 24, 1983.

The June 23, 1983 (day one) sample was 270 ft. from the north edge of the field. Sampling period was 1 hr and 45 minutes.

The June 24, 1983 (day two) sample was 169 ft. from the south edge of the field. Sampling period was 3 hours.

Water samples:

Water samples were taken in the following manner:

1. Background: 1200 ml grab sample
1000 ml composite sample (10-100 ml) from around the pier
2. Flux: composite water samples were collected four times a day during the collection of the flux air samples. Each sample was a composite of 10-40 ml aliquots taken from 10 different locations on the pier.

Petri dish:

Petri dishes (2 dishes per sample) were placed 120 ft. apart along the west edge of the field to determine the application rate. Dishes were also placed on the pier. The dishes were rinsed with several aliquots of methanol and transferred to bottles. The west bank samples were combined and analyzed as a composite sample.

All samples were stored on dry ice for transport to the laboratory where they were stored at -20°C until the time of analysis.

ANALYSIS OF HIGH VOLUME AIR SAMPLES

High volume air samples were analyzed using a method developed by J. E. Woodrow with some modifications. The procedure is outlined below.

1. XAD-4 resin samples were transferred to 500 ml Erlenmeyer flasks and 150 ml of methanol was added. Samples were swirled for two hours and the methanol was decanted into 1000 ml round bottom flasks. An additional 150 ml of methanol was added to the resin and extracted again for two hours. Again the solvent was decanted and 100 ml of methanol was added and swirled for 1.5 hours. Extracts were combined and rotary-evaporated to ca. 10 ml using a water bath temperature of 30°C.
2. Samples were transferred to 250 ml separatory funnels and 100 ml of pH 1.5 - 5% sodium sulfate solution was added. 40 ml of dichloromethane was added also and the contents of the flask partitioned. The dichloromethane layer was filtered over anhydrous sodium sulfate and into a 300 ml round bottom flask. The partitioning process was repeated three times. The combined extract was concentrated to just before dryness. The side of the flask was washed with methanol and the flask contents were evaporated to 1 ml. Four ml of diazomethane was added and the flask was swirled. After 15 minutes, excess diazomethane was removed with a gentle stream of nitrogen. Samples were transferred to sedimentation tubes and volumes adjusted for analysis.
3. The analysis of MCPA and 4-chloro-o-cresol was performed on a Tracor MircoTek 220 with a Dohrmann microcoulometric detector with the following conditions:

Column: 6 ft. \times 1/8 in. 3% SE-30 on 80-100 Chrom W HP AW/DCMS

Temperatures:	injector	230°C
	column	148°C
	outlet block	250°C
	transfer	250°C
	valve	240°C
	oven	830°C

Flow rates:	nitrogen	60 ml/min
	oxygen	100 ml/min

Microcoulometer:	range	450 ohms
	gain switch	high
	gain set	600
	bias set	252 mv
	stir rate	slow
	cell	T-300-S

Chart speed: 40 cm/hr

Sensitivity = 3 ng/m³

Recoveries for both MCPA and 4-chloro-o-cresol (based on a 120 min. at 1.0 m³/min. sample period) are listed in Table 1.

Table 1. Recovery study of XAD-4 resin.

	MCPA (μg)	4-ClOC (μg)	Equivalent (ng/m^3)	% Recovery MCPA	% Recovery 4-ClOC
MMM-IX-74A	5	5	42	85	71
MMM-IX-74B	2	2	17	80	63
MMM-IX-74C	1	1	8.3	62	59

No recoveries were run for 5-chlorosalicylaldehyde (5-ClSA)

ANALYSIS OF WATER SAMPLES

The procedure used for the analysis was from the E.P.A. Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples, Section 10-B. Four modifications were made:

1. Samples were concentrated by use of a roto-evaporator.
2. The water samples were extracted a third time with dichloromethane instead of two extractions.
3. Five ml of methanol was added to the flask before the methylation step.
4. Samples were derivatized using diazomethane instead of 2-chloroethanol.

Procedure:

Samples were frozen until the time of analysis. The volumes were measured, recorded and then added to a one liter separatory funnel. The pH was lowered to ca. 1 with concentrated sulfuric acid (ca. 2 drops). Ten grams of sodium sulfate was added to each funnel and the contents were immediately shaken to prevent clogging the bottom of the funnel. The contents were partitioned three times with dichloromethane and, if necessary, the organic layer was centrifuged. Samples were filtered through anhydrous sodium sulfate and into 300 ml round bottom flasks. The sodium sulfate was washed with 2-25 ml aliquots of dichloromethane. Samples were concentrated to ca. 2 ml via a roto-evaporator. The sides of the flask were washed with three ml of methanol and concentrated to one ml. An additional two ml of methanol was added and the contents were concentrated to one ml. Four ml of diazomethane was added, the flask swirled, and allowed to react for 15 minutes. Excess diazomethane was blown off with a gentle stream of nitrogen. Samples were quantitatively transferred to sedimentation tubes and volumes adjusted for analysis.

Recoveries: two samples fortified at 14 ppb were run with recoveries of 73 and 75 percent for MCPA. No recoveries were performed for the 4-chloro-o-cresol. Water samples were not analyzed for 5-chlorosalicylaldehyde.

CALCULATION OF FLUX

The flux was calculated using the following equations.

$$R_i = \frac{g \left(\frac{dT}{dZ} + r \right)}{T \left(\frac{dU}{dZ} \right)^2} \quad \text{EQ. (1)}$$

$$\phi = (1 \pm 16R_i)^{\pm 0.33} \quad \text{EQ. (2)}$$

$$P = k^2 \frac{(c_1 - c_2)(U_2 - U_1)}{\phi^2 \left[\ln \left(\frac{Z_2 - D}{Z_1 - D} \right) \right]^2} \quad \text{EQ. (3)}$$

c is pesticide concentration in mg/cm³

T in degrees K

Z is vertical height in cm

D is the height between the ground and the top of the crop; for water it is zero

r is the dry adiabatic lapse rate: = 9.86×10^{-5} °K/cm

g is the acceleration due to gravity: = 980 cm/sec²

U is the windspeed in cm/sec

R_i is known as the Richardson number and may be positive or negative.
(+ = stable conditions, - = unstable conditions)

P is flux at the higher sampling point in mg/cm²/sec

k is von Karman constant = 0.4

If R_i is stable, then $\phi = (1 + 16R_i)^{0.33}$; if unstable then $\phi = (1 - 16R_i)^{-0.33}$

The flux (vertical) is presented in Table 6. The units are in ng/cm²/hr.

Bolero Flux Data

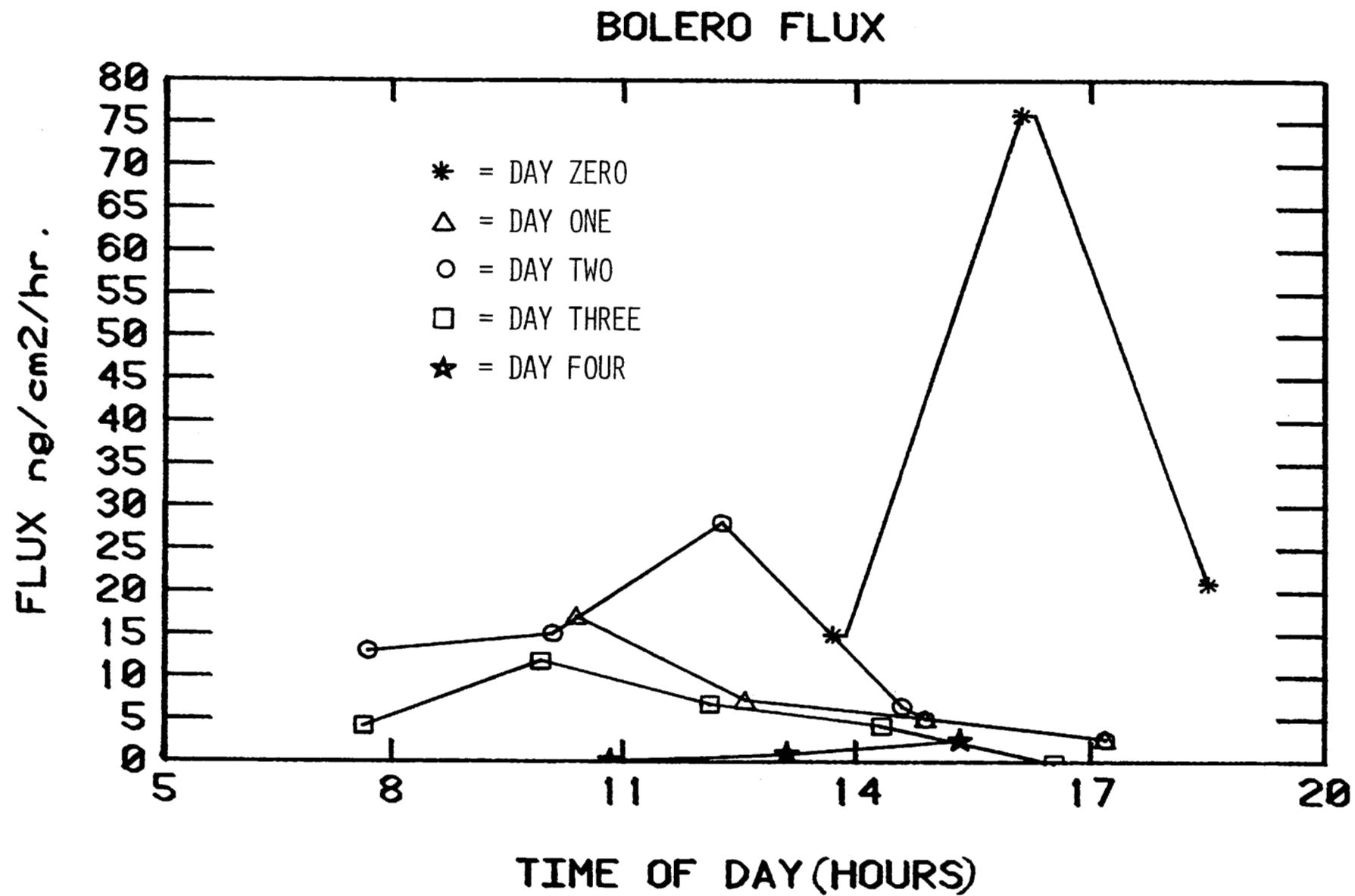
Bolero flux samples were taken from May 30, 1983, to June 4, 1983, using the procedures outlined for the MCPA samples. The CDFA chemistry laboratory analyzed the resin for Bolero.

DATA USED FOR BOLERO FLUX

Day	Time	High °C Temp	Low °C Temp	High mph wind speed	Low mph wind speed	High ng/m ³ Bolero	Low ng/m ³ Bolero
0	1:42	29.3	29.3	10	8	180	790
0	4:07	31.5	31.8	12	8	666	2166
0	6:31	29.0	29.4	8.8	7.5	347	1217
1	10:26	21.0	21.5	7.0	5.3	83	688
1	12:38	24.5	24.6	5.0	4.0	243	739
1	14:52	26.5	26.6	5.0	4.0	305	652
1	17:12	26.0	26.0	8.7	6.7	304	1391
2	7:42	18.2	19.3	7.7	5.7	244	553
2	10:05	21.3	22.8	6.7	5.7	181	517
2	12:20	23.1	24.2	10.0	7.7	258	905
2	2:36	22.4	22.8	12.3	7.0	344	1260
3	7:37	16.9	17.4	6.0	5.3	104	278
3	9:53	20.3	21.0	4.3	3.7	129	517
3	12:08	23.0	24.1	4.3	3.7	301	474
3	2:17	26.1	26.6	5.0	3.3	198	345
3	4:30	27.4	27.8	3.0	4.3	102	517
4	10:45	25.9	25.9	4.7	3.7	635	593
4	1:08	29.0	28.5	4.7	5.0	211	275
4	3:17	29.3	28.8	4.3	5.7	257	1009

BOLERO FLUX: HIGH VOLUME AIR SAMPLE

<u>DAY</u>	<u>TIME</u>	<u>FLUX ng/cm²/hr</u>
0	13:42	15.0
0	16:07	76.0
0	18:31	21.0
1	10:26	17.0
1	12:38	7.2
1	14:52	5.0
1	17:12	2.6
2	7:42	13.0
2	10:05	15.0
2	12:20	28.0
2	14:36	6.5
3	7:37	4.4
3	9:53	12.0
3	12:08	7.0
3	14:17	4.4
3	16:30	0
4	10:45	-0.54
4	13:08	0.82
4	15:17	2.4



Ordram Flux Data

Ordram flux samples were taken from June 6, 1983, to June 9, 1983, using the procedures outlined for the MCPA samples. The CDFA chemistry laboratory analyzed the resin for Ordram.

DATA USED FOR ORDRAM FLUX

Day	Time	High °C Temp	Low °C Temp	Wind speed high (MPH)	Wind speed Low (MPH)	Ordram high µg/m ³	Ordram low µg/m ³
0	7:30	26.8	27.5	14.0	10.7	2.8	6.6
0	16:45	36.4	37.8	3.0	2.3	28	47
0	18:50	34.2	35.4	3.0	2.3	25	49
1	7:00	23.6	24.0	3.3	4.0	9.8	18
1	9:00	28.7	30.4	2.0	1.3	4.2	11
1	11:00	30.1	30.7	2.3	2.0	5.9	12
1	13:00	31.8	31.8	3.3	4.0	-	20
1	15:05	34.5	34.5	5.0	5.3	15	30
1	17:00	34.5	34.5	6.0	3.3	19	23
2	7:00	17.8	19.1	6.7	2.7	3.3	9.3
2	9:05	22.1	22.7	6.0	4.0	5.9	9.3
2	11:05	27.7	28.0	5.3	4.3	7.6	11
2	13:05	30.7	31.0	5.0	3.7	6.8	9.3
2	15:05	30.4	30.5	7.3	4.7	11	17
2	17:00	29.7	29.7	9.3	6.0	13	19
3	7:00	17.7	18.5	5.0	3.3	3.3	-
3	9:05	19.4	20.4	4.3	3.6	3.2	3.9
3	11:00	25.3	23.5	3.7	3.3	3.7	-
3	13:00	29.6	30.1	7.3	5.3	8.5	8.5
3	15:00	30.8	31.1	8.3	5.3	9.6	12
3	17:00	30.3	30.5	9.3	5.7	6.1	8.9

Ordram flux samples were taken from July 6, 1983, to June 9, 1983, using the procedures outlined for the MCPA samples. The CDFA chemistry laboratory analyzed the resin for Ordram.

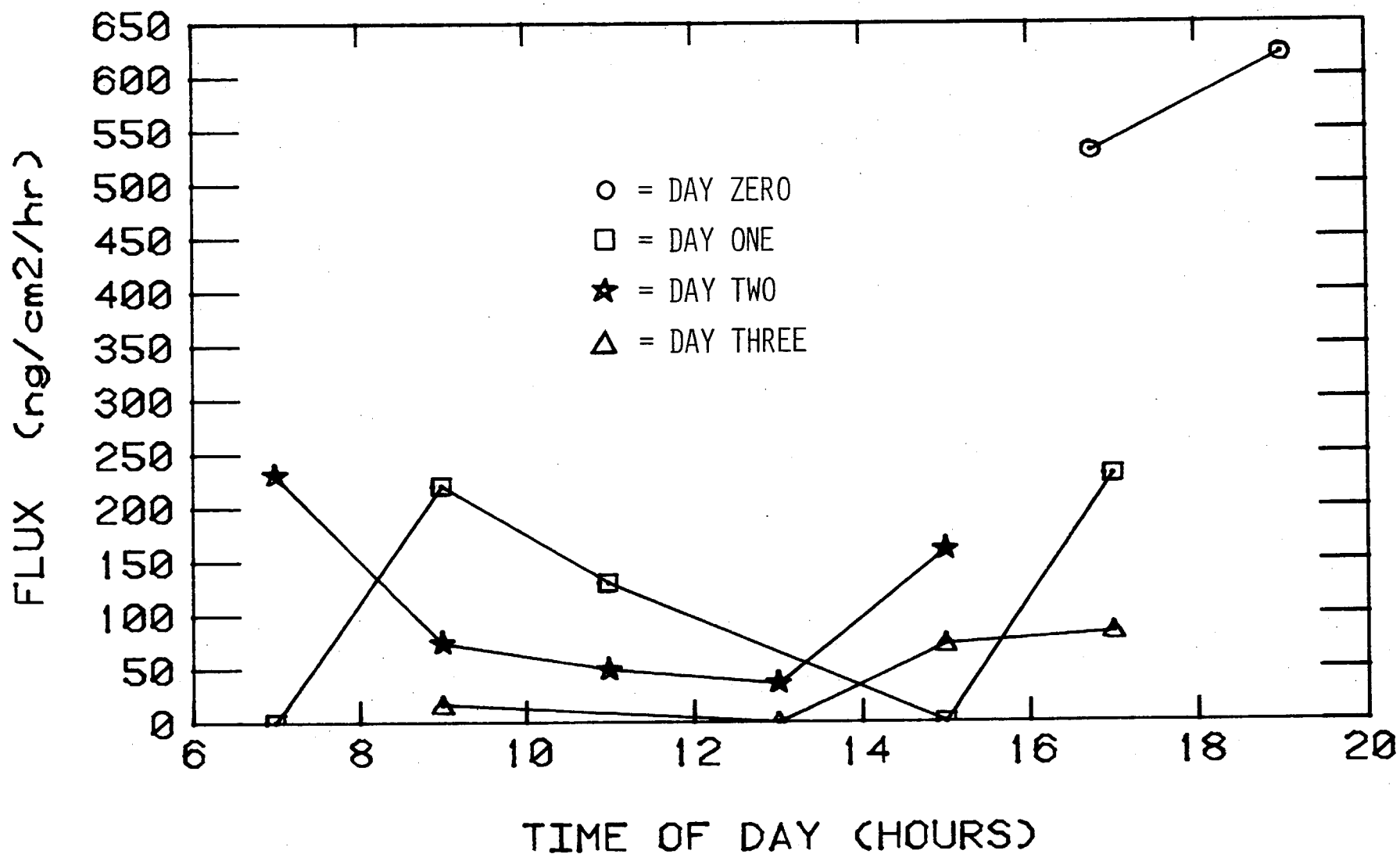
ORDRAM FLUX $\text{ng}/\text{cm}^2/\text{hr}$

<u>DAY</u>	<u>TIME</u>	<u>FLUX $\text{ng}/\text{cm}^2/\text{hr}$</u>
0	7:30	80
0	16:45	530
0	18:50	620
1	7:00	-100
1	9:00	220
1	11:00	130
1	15:05	-24
1	17:05	230
2	7:00	230
2	9:05	74
2	11:05	49
2	13:05	36
2	15:05	160
3	9:05	17
3	13:00	0
3	15:00	73
3	17:00	84

1/13/83

ORDRAM FLUX

94



A P P E N D I X B

Chain of Custody for Chemical Analyses

STATE OF CALIFORNIA
DEPARTMENT OF
AND AGRICULTURE

CHAIN OF CUSTODY RECORD
(Use ball point pen only)

ENVIRON. MONITOR. & PEST MGMT
ENVIRON. HAZARDS ASSESSMENT
1220 N STREET, ROOM A-149
SACRAMENTO, CA 95814

Study #	Sample #	Sampling Date						Person Collecting	Location			KEY	Key Sample Type	Water (cm) Depth	Water (°C) Temp.	Air (°C) Temp.	Rel. Hum. (%)																						
		Mo	Day	Yr	Time On	Time Off	Field		Paddy	Site																													
-	-	2	0																																				
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40

Lab #	KEY																																						
	Molinate		Units	Sulfoxide		Thiobencarb		Sulfoxide		MCPA		Cresol																											
41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80

Location:	Lab Results:		SAVE EXTRACTS	
Remarks:	Molinate (Ordram)			
	Sulfoxide			
	Thiobencarb (Bolero)			
	Sulfoxide			
	MCPA			
	Cresol			
	Chemist	Date		
	Relinquished by: (Signature)	Date/Time		
	Received by (Signature)	Relinquished by (Signature)	Date/Time	
	Received by (Signature)	Relinquished by (Signature)	Date/Time	
	Received by (Signature)	Relinquished by (Signature)	Date/Time	
KEY	Sample type:	Received for Laboratory by: (Signature)	Date/Time	Lab #
Period:	CAG=Cage Fallout			
B=Background	FAL=CDFA Fallout			
S=Spray	HIV=Hi-vol			
P=Post spray	LOV=Lo-vol			
	SOI=Soil			
Units:	VEG=Vegetation			
U=Micrograms	WAT=Water			
M=ppm				
B=ppb				

Distribution: Original and one copy accompanies shipment, one copy to Field files.

A P P E N D I X C

Chemical Analytical Methods for Thiobencarb, Molinate, and Their
Breakdown Products in Water, Soil, Vegetation, and Air Samples.

CALIFORNIA DEPT. OF FOOD & AGRIC.
ENVIRONMENTAL MONITORING SECTION
CHEMISTRY LABORATORY SERVICES
3292 Meadowview Road
Sacramento, CA 95832
(916)+323-5814/5815

Original Date:9/21/83
Supersedes: NEW
Current Date:9/21/83
Method #:67.0

RICE HERBICIDES IN WATER

SCOPE:

Analysis of Water for Bolero, Bolero Sulfoxide, Ordram and Ordram Sulfoxide.

PRINCIPLE:

The water is extracted with Dichloromethane. The solvent is evaporated to dryness on a rotary evaporator. The residue is brought to volume with Methanol and analyzed by GC (Bolero, Ordram) and HPLC (Sulfoxides)

REAGENTS AND EQUIPMENT:

Dichloromethane (Pesticide Quality)
Methanol (U.V. Grade)
Sodium Sulfate anhydrous
1000ml Separatory funnels
15cm Column Funnels
500ml Round Bottom Evaporating Flasks
Rotary Evaporator
H.P.L.C. (Perkin Elmer Series 4, U.V. detector, Autosampler)
G.C. (Varian 3700, TSD Detector, Autosampler)

ANALYSIS:

- 1) 800 grams of water sample is poured into a 1000ml separatory funnel.
- 2) 50 mls of Dichloromethane is added and sample shaken for 1 minute
- 3) Organic layer is drained through filter with 20grams anhydrous Sodium Sulfate into a 500ml Round bottom flask.
- 4) Steps 2 & 3 are repeated twice more.
- 5) Dichloromethane is evaporated to dryness on a Rotary vacuum evaporator with 30 degree centigrade water bath.
- 6) Residue is brought to volume (5mls) with Methanol.
- 7) Analyze the extract on GLC and HPLC.

DESORPTION COEFFICIENT:

EQUIPMENT CONDITIONS:

ORDRAM SULFOXIDE: BOLERO SULFOXIDE

Perkin Elmer Series 4 HPLC with Kratos variable wavelength UV detector. Perkin Elmer ISS100 Autosampler (20ul injection)
12.5cm 5u C18 Column (Brownlee Labs), Reverse Phase.
Flow= 1.2mls/minute; Oven=40 Cent; 45% methanol 55% H2O
220nm ; 1x5mv/fs

BOLERO:ORDRAM

Varian 3700 GC ;TSD detector;Autosampler

30meter SE54 Capillary column ;100:1 split

Oven initial=100C (2min hold)10C/min Final=270C

Injector=250C Detector=250C

Perkin Elmer Series 4 HPLC With Kratos variable wavelensth

UV detector.P.E. ISS100 Autosampler

12.5cm 5um C18 Column (Brownlee Labs);Reverse Phase

75% MeOH 25% H2O : 1.0mls/min

CALCULATIONS:

(Area Sample)(NG Std)(Final Volume mls)(1000)
PPB Herbicide=-----
(Area Standard)(UL Sample injected)(Weight H2O)

DISCUSSION:

Recoveries and Sensitivities

(Sensitivities may vary with sample interferences)

Bolero ,Ordram (95%; Minimum Detectable Level =5ppb

Bolero Sulfoxide (90%;MDL 10ppb)

Ordram Sulfoxide (80%;MDL 10ppb)

REFERENCES:

- 1)PERSISTENCE AND FACTORS AFFECTING DISSIPATION OF MOLINATE
Duel et al : J.Environ. Qual. :Vol 17,No 3,1978
- 2)ORDRAN IN SOAP AND WATER HANDWASHES
Fredrickson:Dept. Food and Asriculture:Method 37.1
- 3)DETERMINATION OF THIOBENCARB IN WATER
FuJie:Chevron Chemical Co.:Method RM-16W-2 (1983)
- 4)VOLATILIZATION OF BENTHIOCARB FROM AQUEOUS SOLUTION
Ishikawa et al:J.Pesticide Sci.:Vol 2 (1977)
- 5)DISSIPATION OF MOLINATE IN A RICE FIELD
Soderquist:Asric.&Food Chemistry:Vol.25 #4 (1977)

WRITTEN BY: Richard R. Maykoski

TITLE: Asricultural Chemist I

REVISED BY:

TITLE:

APPROVED BY: David Conrad

TITLE: Asricultural Chemist III

CALIFORNIA DEPT. OF FOOD & AGRIC.
ENVIRONMENTAL MONITORING SECTION
CHEMISTRY LABORATORY SERVICES
3292 Meadowview Road
Sacramento, CA 95832
(916)+323-5814/5815

Original Date:9/30/83
Supersedes: new
Current Date:9/30/83
Method #:68.0

RICE HERBICIDES IN SOIL

SCOPE:

Analysis of rice field soil samples for Bolero and Ordram.

PRINCIPLE:

A representative sample aliquot is extracted with acetone:water. The Acetone is removed in a rotary vacuum evaporator and the acidified water extracted with Dichloromethane. The solvent is evaporated under vacuum and sample brought to volume with methanol. The extract is analyzed by GLC.

REAGENTS AND EQUIPMENT:

Rotary Tumbler
Rotary Vacuum Evaporator
Dichloromethane (Pesticide Grade)
Acetone (Pesticide Grade)
Methanol (Pesticide Grade)
Sodium Sulfate (Anhydrous)
250ml Separatory Funnels
Column Filters
1000ml Round Bottom Flasks
500ml Round Bottom Evaporating Flasks
90mm Glass Buchner Funnels
500ml Side Arm Vacuum Flasks
500ml Wide Mouth Amber Jars
Varian 3700 GC with TSD detector and 30meter SE54 Capillary column.
Cuisinart Blender

ANALYSIS

MOISTURE ANALYSIS

- 1) A representative 10 gram portion is weighed to the nearest milligram in an aluminium weighing dish.
- 2) The dish is heated in an oven (105C) for 12 hours.
- 3) The dish is removed and allowed to cool to room temperature in a desiccator.
- 4) The dish and dry soil is reweighed to the nearest milligram

EXTRACTION

- 1) Entire sample is placed in Cuisinart blender and mixed to obtain homogeneous sample.
- 2) 100 gram portion is placed in 500ml wide mouth Jar along with 40mls distilled water; 150mls Acetone; 5mls 2N NaOH.
- 3) Sample is tumbled for 40 minutes on rotary tumbler, removed, and allowed to settle for 20 minutes.
- 4) Sample is poured SLOWLY into a 90mm glass Buchner funnel on a 500ml side arm vacuum flask.
- 5) Soil collected on filter is allowed to dry and then returned to its sample bottle along with filter paper.
- 6) Add 100mls Acetone; 30mls distilled water; 6mls 2N H2SO4 to sample and return to tumbler for an additional 20 minutes.
- 7) Let soil settle for 20 minutes and pour SLOWLY through the

Buchner funnel.

- 8) Wash Jar and funnel with 50mls Acetone.
- 9) Transfer solvent to 500ml round bottom evaporating flask and rotoevaporate the Acetone under vacuum (40°C Centigrade)
- 10) Acidify the sample to pH3 with 10N H2SO4.
- 11) Transfer the sample to a 250ml separatory funnel rinsing the flask with 25mls distilled water.
- 12) Extract the sample three times with 30mls Dichloromethane each time. Drain the organic layer into a 250ml round bottom flask through a column funnel filled with 25 grams anhydrous Sodium Sulfate.
- 13) Place on Rotary Vacuum Evaporator (30°C Centigrade) and evaporate to 1ml. Add 1ml Methanol and continue evaporating until all Dichloromethane is gone.
- 14) Transfer to volumetric flask and bring sample to 5mls final volume with Methanol.
- 15) Submit extract for analysis by GLC.

DESORPTION COEFFICIENT:

EQUIPMENT CONDITIONS:

Varian 3700 GC ; TSD Detector ; Autosampler
30 meter SE54 Capillary Column ; 100:1 split
Oven initial = 100C (2min hold) 10C/min Final = 270C
Injector = 250C Detector = 250C

CALCULATIONS:

$$\% \text{ Moisture} = \frac{(\text{Dry Weight} - \text{Tare Weight}) \times 100\%}{(\text{Wet Weight} - \text{Tare Weight})}$$

$$\text{PPM Herbicide} = \frac{(\text{Peak Height Sample})(\text{NG Std})(5\text{mls})}{(\text{Peak Height Standard})(\text{Sample Wt})(1 - \% \text{Moist}/100)}$$

DISCUSSION:

RECOVERIES

Ordram: 100% at 0.1 to 3.0 PPM levels

Bolero: 80% to 100% at 0.1 to 3.0 PPM levels

SENSITIVITIES

Ordram & Bolero: Minimum Detectable Level = 0.05 PPM

REFERENCES:

- 1) PERSISTENCE AND FACTORS AFFECTING DISSIPATION OF MOLINATE
Duel et al: J. Environ. Qual.: Vol 17, No 3, 1978
- 2) ORDRAM IN SOAP AND WATER HANDWASHES
Fredrickson: Dept. Food and Agriculture: Method 37.1
- 3) DETERMINATION OF THIOBENCARB IN WATER
Fujie: Chevron Chemical Company: Method RM-16W-2 (1983)
- 4) VOLATILIZATION OF BENTHIOCARB FROM AQUEOUS SOLUTION
Ishikawa et al: J. Pesticide Sci.: Vol 2 (1977)
- 5) DISSIPATION OF MOLINATE IN A RICE FIELD

WRITTEN BY: RICHARD MAYKOSKI

TITLE: AGRICULTURAL CHEMIST 1

REVISED BY:

TITLE:

APPROVED BY: David Conrad

TITLE: Agricultural Chemist III

CALIFORNIA DEPT. OF FOOD & AGRIC.
ENVIRONMENTAL MONITORING SECTION
CHEMISTRY LABORATORY SERVICES
3292 Meadowview Road
Sacramento, CA 95832
(916)+323-5814/5815

Original Date:4/13/84
Supercedes: new
Current Date:4/13/84
Method #: 79.0

ANALYSIS OF RICE FOLIAGE FOR HERBICIDES

SCOPE:

Analysis of rice foliage for Bolero, Ordram, Bolero Sulfoxide and Ordram Sulfoxide.

PRINCIPLE:

The sample is blended with dichloromethane and filtered. The solvent is evaporated to dryness on a rotary vacuum evaporator. The residue is brought to final volume with hexane and analyzed by GLC.

REAGENTS AND EQUIPMENT:

Dichloromethane (Pesticide Grade)
Hexane (Pesticide Grade)
Sodium Sulfate (Anhydrous)
Blender (Sorvol Omni Mixer)
Filter Paper (Sharkskin 70mm)
Funnel (70mm Buchner)
Vacuum Flask (500ml side-arm)
250ml Round Bottom Flasks
Varian 3700 Gas Chromatograph w/ TSD detector

ANALYSIS:

- 1) Cut and weigh sample (~40grams) into one pint mason jar.
- 2) Add 90mls dichloromethane and 30grams anhydrous sodium sulfate.
- 3) Blend on high speed in an ice bath for 2 minutes.
- 4) Place 70mm Buchner Funnel with filter paper onto 500ml suction flask
- 5) Add blended contents of jar to funnel and filter.
- 6) Rinse filter with 30mls dichloromethane.
- 7) Transfer solvent to a 250ml round bottom flask and evaporate to dryness on a rotary vacuum evaporator (20mm Hg, 35 C)
- 8) Add 10mls hexane to flask and evaporate to dryness as above.
- 9) Transfer to a volumetric test tube with hexane and bring to final volume (5mls).
- 10) Submit extract for GLC analysis.

DESORPTION COEFFICIENT:

EQUIPMENT CONDITIONS:

Varian 3700 Gas Chromatograph with Thermionic Detector
Varian 8000 Autosampler (4 ul injection)
Hewlett Packard crosslinked 5% phenylmethyl silicone fused silica
column (25 meter, 0.33 um film, 0.2 mm i.d.)
Column Temperature initial=100 C (2min hold);10 C/min;final=240 C
Injector Temperature=240 C ; Detector Temperature=250 C
H2=4.0 mls/min ; Air=160 mls/min ; Carrier Gas=0.8mls/min
Bead=4.00 ; 4ul Autosampler injection (split mode 50:1)

CALCULATIONS:

(Peak ht sample)(NG Standard)(5 mls)
PPM Herbicide = -----
(Peak ht standard)(Sample weight gms)

DISCUSSION:

RECOVERIES

Ordram, Bolero- 80-100% at 0.1 to 5.0PPM
Ordram Sulfoxide- 70-90% at 0.5 to 5.0PPM
Bolero Sulfoxide- 80-100% at 0.5 to 5.0PPM

SENSITIVITIES (40 gram sample)

Ordram, Bolero-MDL =0.05ppm
Ordram Sulfoxide, Bolero Sulfoxide- MDL \approx 0.5PPM

REFERENCES:

DISSIPATION OF MOLINATE IN A RICE FIELD
Soderquist et al:Agricultural and Food Chemistry:V25 #4 p940-945
VOLATILIZATION OF BENTHIOCARB FROM AQUEOUS SOLUTIONS
Ishikawa et al:J. Pesticide Sci : Vol 2 (1977)
PERSONAL DISCUSSIONS
Scott Fredrickson:CA Dept. Food & Agriculture
James Echelberry:CA Dept Food & Agriculture

WRITTEN BY: Richard Maykoski

TITLE: Agricultural Chemist I

REVISED BY:

TITLE:

APPROVED BY: David Conrad

TITLE: Agricultural Chemist III

CALIFORNIA DEPT. OF FOOD & AGRIC.
ENVIRONMENTAL MONITORING SECTION
CHEMISTRY LABORATORY SERVICES
3292 Meadowview Road
Sacramento, CA 95832
(916)+323-5815/5814

Original Date: 4/23/84
Supersedes: NEW 77.1
Revision #: -----

TITLE: HI-VOLS (RICE HERBICIDES)

SCOPE: ANALYSIS OF AIR HI-VOLS FOR BOLERO, ORDRAM AND THEIR SULFOXIDES

PRINCIPLE: The XAD-2 resin is extracted by sonication with Acetone in 500 ml amber jars. The solvent and two rinses are suction filtered, evaporated and brought to final volume. Extract is analyzed by GLC (NPD)

REAGENTS AND EQUIPMENT:

500ML AMBER WIDE MOUTH JARS
90mm Buchner funnels
1000ML Round bottom evaporating flasks
Rotary evaporator w/water bath and vacuum pump
Acetone-Pesticide grade
Ultrasonic water bath
90mm filter paper (Sharkskin)
1 liter side-arm vacuum flasks

ANALYSIS:

Sample is quantitatively transferred to 500ml amber jars.
Enough Solvent to cover resin was added (~200mls)
Samples were placed in Ultrasonic Bath (30C) for 30 minutes
Resin was poured into 19mmx500mm glass columns (3" anhydrous Sodium Sulfate)
Resin is eluted with 400mls solvent
Solvent is collected in 1000ml flask
Solvent was evaporated to dryness on Rotovap (35 C)
The sample was brought to final volume (5mls) with Hexane
The extract was submitted for GLC analysis

CALCULATIONS

$$\text{UG/SAMPLE} = \frac{\text{PK Height Sample} \times \text{ng Std} \times \text{Sample Vol}}{\text{PK Height Standard} \times \text{UL sample}}$$

DISCUSSION

RECOVERIES

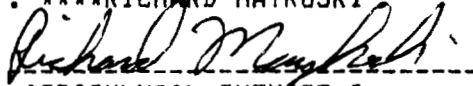
Bolero: 95% at 50ug/sample
Ordram: 80% at 50ug/sample
Bolero Sulfoxide: 45% at 50ug/sample
Ordram Sulfoxide: 70% at 50ug/sample

EQUIPMENT CONDITIONS

Varian 3700 Gas Chromatograph with Thermionic Detector
Varian 8000 Autosampler (4ul injection; split 100:1)
Hewlett Packard crosslinked 5% phenylmethyl silicone fused
silica column(25 meter, 0.33um film, 0.2mm i.d.)
Column Temperature initial=100 C(2min); 10 C/min; final=240 C
Injector Temperature=240 C ; Detector Temperature=250 C

REFERENCES:

WRITTEN BY: ****RICHARD MAYKOSKI

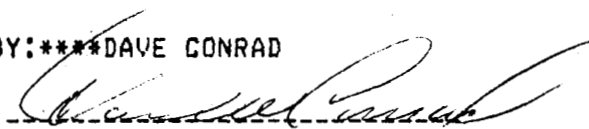


TITLE: ****AGRICULTURAL CHEMIST I

REVISED BY:****

TITLE: ****

APPROVED BY:****DAVE CONRAD



TITLE:****AGRICULTURAL CHEMIST III

CALIFORNIA DEPT. OF FOOD & AGRIC.
ENVIRONMENTAL MONITORING SECTION
CHEMISTRY LABORATORY SERVICES
3292 Meadowview Road
Sacramento, CA 95832
(916)+323-5815/5814

Original Date: 3/5/84
Supersedes: NEW 77-2
Revision #: -----

TITLE: LO-VOLS (BOLERO, ORDRAM)

SCOPE: ANALYSIS OF RICE HERBICIDES ON AIR LO-VOLS

PRINCIPLE: The tubes are extracted with acetone, concentrated and analyzed by GLC (NPD)

REAGENTS AND EQUIPMENT:

250ML Round bottom evaporating flasks
Rotary evaporator w/water bath and vacuum pump
ACETONE - Pesticide grade
HEXANE - Pesticide grade
125ml Separatory funnels

ANALYSIS:

The tubes are clamped in a vertical position.
A 250 ml separatory funnel is placed above tube and a 250ml round bottom flask under the tube.
100mls Acetone is added to funnel and dripped thru the tube at a flow rate of 1ml/minute.
The excess Acetone is blown out of the tube with compressed air into the round bottom flask.
The acetone is evaporated to dryness on a rotary evaporator (35 C and 20 inches HG vacuum)
The residue is dissolved in hexane and brought to final volume (5mls)
The extract is analyzed on GC (NPD)

CALCULATIONS

UG/SAMPLE =
$$\frac{\text{PK Height Sample} \times \text{ns Std} \times \text{Sample Vol}}{\text{PK Height Standard} \times \text{UL sample}}$$

DISCUSSION

RECOVERIES

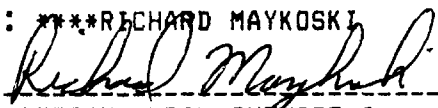
Bolero: 95% at 5 to 50us/sample
OrDRAM: 80%-90% at 5 to 50us/sample
Bolero Sulfoxide: 50% at 10us/sample
OrDRAM Sulfoxide: 70% at 10us/sample

EQUIPMENT CONDITIONS

Varian 3700 Gas Chromatograph with Thermionic Detector
Varian 8000 Autosampler (4ul injection)
Hewlett Packard crosslinked 5% phenylmethyl silicone fused
silica column (25 meter, 0.33um film, 0.2mm i.d.)
Column Temperature initial=100C(2min hold); 10C/min; final=240
Injector Temperature=240C ; Detector Temperature=250 C
4ul autosampler injection(split 50:1)

REFERENCES:

WRITTEN BY: ***RICHARD MAYKOSKI

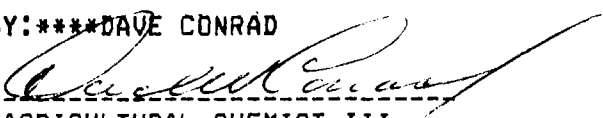


TITLE: ****AGRICULTURAL CHEMIST I

REVISED BY:****

TITLE: ****

APPROVED BY:****DAVE CONRAD



TITLE:****AGRICULTURAL CHEMIST III

A P P E N D I X D

Chain of Custody for Flow Fields

STATE OF CALIFORNIA
DEPARTMENT OF FOOD
AND AGRICULTURE

CHAIN OF CUSTODY RECORD
(Use ball point pen only)

ENVIRON. MONITOR. & PEST MGMT.
ENVIRON. HAZARDS ASSESSMENT
1220 N STREET, ROOM A-149
SACRAMENTO, CA 95814

Study #				Date			Time		Person collecting		Location			Companion Water Sample		Water depth (cm)		Water temp. (°C)		Air temp. (°C)		Rel. hum. (%)																	
				Mo	Day	Yr					Field	Paddy (I or D)	Site																										
-	F	2	0				8	3																															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40

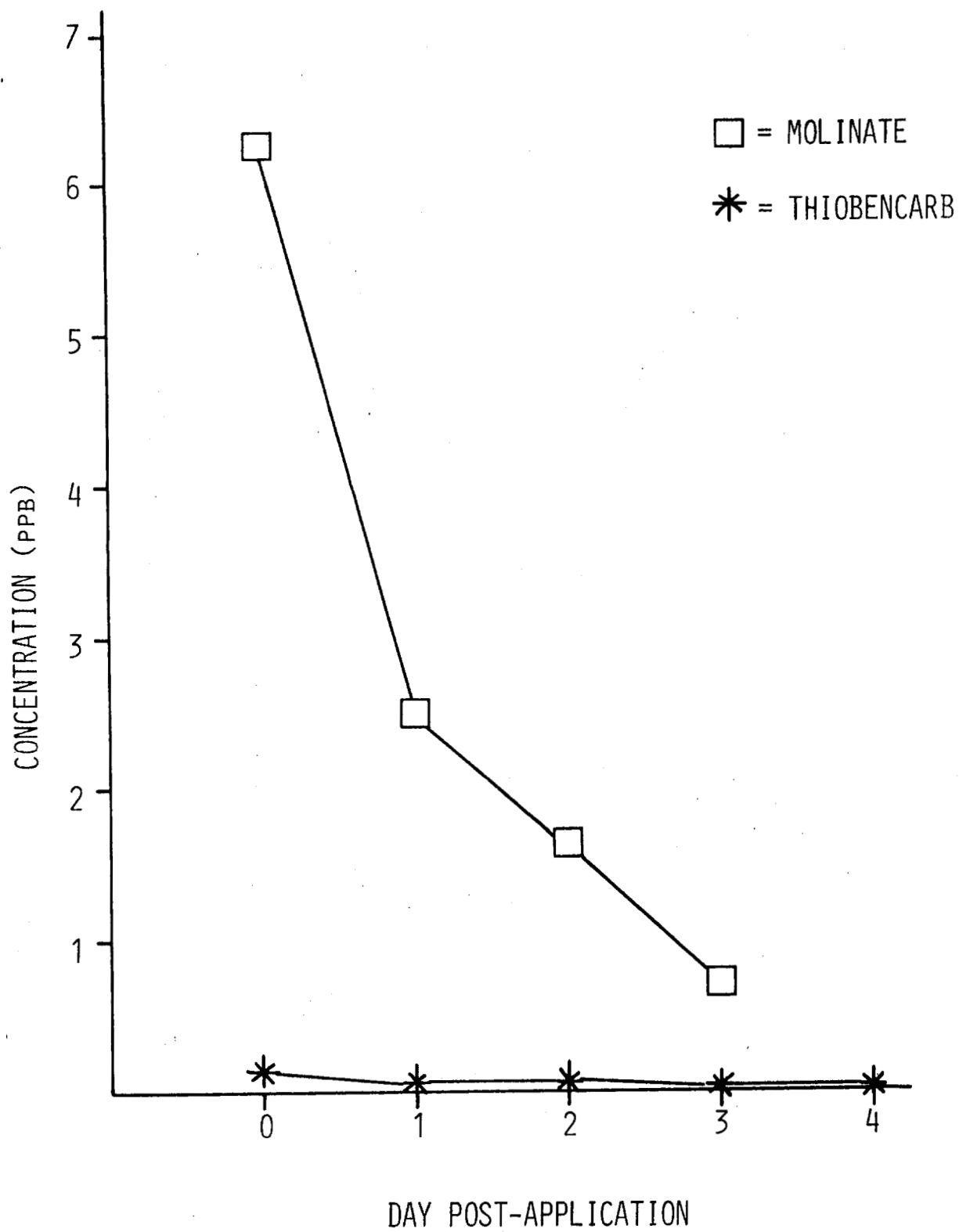
INLET												DRAIN											
Weir 1		Weir 2		Weir 3		Weir 1		Weir 2		Weir 3		Weir 1		Weir 2		Weir 3							
Weir Width	Staff Gauge Reading	Weir Width	Staff Gauge Reading	Weir Width	Staff Gauge Reading	Weir Width	Staff Gauge Reading	Weir Width	Staff Gauge Reading	Weir Width	Staff Gauge Reading	Weir Width	Staff Gauge Reading	Weir Width	Staff Gauge Reading	Weir Width	Staff Gauge Reading						
(in)		(in)		(in)		(in)		(in)		(in)		(in)		(in)		(in)							
41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58						
59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76						
77	78	79	80																				

REMARKS:

A P P E N D I X E

Comparison of Thiobencarb and Molinated Concentrations in Air.

CONCENTRATIONS OF MOLINATE AND
THIOBENCARB IN AIR OVER TIME



A P P E N D I X F

E R R A T A

Environmental Fate of Selected Rice Herbicides (Thiobencarb and Molinate)
Under Field Conditions. April 1984

E R R A T A

page iii Paragraph 2, Section 108 should be replaced with Section 208.

Paragraph 4 should be replaced with the following:

Special thanks are extended to the agricultural commissioners and staff in Colusa and Glenn Counties for their assistance; to Lou Hoskey, Glenn-Colusa Irrigation District, for his help with water flow measurements, interpretive charts and the use of a Stevens Staff Gauge; and to Jack Campbell, Kanawa Irrigation District, for helping to identify suitable fields to monitor.

page 11 The second line on this page should be replaced with

$$\text{Kg of thiobencarb in vegetation} = \frac{d a c}{1 \times 10^{12}}$$

where: d=denstiy of vegetation (g/cm²)

a=area of the field (cm²)

$$\text{Kg of thiobencarb in air} = \frac{f a h}{1 \times 10^{12}}$$

where: f=evaporative flux (ng/cm²/h)

h=hours in a day

page 20 In Figure 11, replace Δ = air/vegetation

with Δ = air/water

pages 28-32 In all these figures replace [(ppb/sec)/ha]

and

60-68

with [ug/sec/ha]

Page 70 In Table 11, replace Log of Day with (Log of Day + 1) in all equations.

In footnote a/ replace thiobencarb with molinate.